Heritage wrought iron: towards the development of evidence based standards for coating

Nicola J. Emmerson

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Summary

Effective management of heritage assets relies on decision-making which is underpinned by empirical evidence of impact of treatments on long term survival prospects of materials. Historic wrought iron presents a particular problem for conservation. It occupies a niche position between heritage and engineering, is frequently exposed to outdoor atmospheric corrosion and, in the case of bridges, gates and similar structures, may be required to perform a distinct function. Sector guidance to direct practices is based on anecdotal evidence and established methods. British Standards relate to modern steels hence application to historic ferrous metals is complicated by differences in metallurgy and lack of concession to conservation ethics.

This study generates empirical evidence of the effects of five surface preparation methods and three protective coating systems on the corrosion rate of historic wrought iron samples. Immersion in sodium hydroxide solution and blasting with crushed walnut shells are found to reduce corrosion rates of uncoated wrought iron. Aluminium oxide and glass beads blasting increase corrosion rate but offer removal of contaminants and a keyed surface for coating adhesion. Flame cleaning increases corrosion rate by almost four times the uncleaned wrought iron corrosion rate.

A two-pack epoxy resin coating system with polyurethane topcoat applied over substrate surfaces blasted to Sa2.5 (near white metal) and a surface tolerant single-pack alkyd coating applied over coherent oxide layers successfully prevented corrosion for almost two years in high static relative humidity environments. An alkyd system applied over Sa2.5 blasted surface does not significantly reduce corrosion rate of the uncoated substrate. A cost benefit approach to interpreting the empirical results in relation to practicalities of applying the treatments is advocated.

The methods developed for standardising historic sample material and measuring oxygen consumption of coated samples as proxy corrosion rate offer scope for further work in this area. A standardised approach to testing permits correlation of test data between workers in this area to generate a database of empirical data to inform decision-making.

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Dedication

For James Donald Emmerson, Christopher John Mannion and Reuben Jung Karki.

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1 Introduction

1.1 The nature of historic wrought iron

1.1.1 Production and standardisation

Modern production processes are designed to deliver material outputs that are standardised, uniform in appearance and composition, predictable in properties and responses, mass producible and guaranteed to perform over a specified and predetermined period. Many are ultimately disposable and intended to require minimal maintenance during their useful lifetime. This approach fits with societal expectations of predictability, ease of use, fit-for-purpose, minimum intervention until wholesale replacement and a money back guarantee in case of early failure. Industry and engineering also work in this manner with components engineered for minimum maintenance and periodic replacement.

Having as its raison d'être the preservation of archaeological and historic objects in perpetuity, conservation cannot buy into this disposable culture. Failures of materials must be prevented and deterioration rates reduced to a bare minimum. A running battle against agents of decay is fought with little financial support for research into appropriate materials, treatments and environments. All this must be achieved within the constraints of professional ethics. The process is made all the more difficult by the nature of the wide range of historic materials it deals with which are not standardised and predictable in the manner of their modern counterparts.

The production of archaeological and historic wrought iron is a case in point. Numerous histories, chronologies and studies detail developments up to the 20th century (Tylecote 1976; Starley 1999; O'Sullivan and Swailes 2009; Merriman 1958; Hooper et al. 2003; McDonnell 1989; Charlton et al. 2012; Rehren et al. 2013; Aston and Story 1939; Wallis and Bussell 2008; Lyon 2010, 1695; Scott and Eggert 2009) highlighting changing methods with technological advances and resultant change in material composition and properties. Reduction of iron from its ore was originally a small scale batch process for domestic, utilitarian objects. Furnace temperatures well below the melting point of iron (1540°C) produced a solid bloom of iron, siliceous slag and other waste materials. Hand working removed much of the slag with the remainder distributed in stringers. Growing in scale to meet the requirements of the Roman military and a broader range of domestic and civic objects, it remained a batch process with smelt halted to remove the bloom until the development of the blast furnace in the late 16th/ early 17th centuries. Increased fuel: ore ratios created more reducing atmospheres carburising the iron, reducing its melting point to 1200°C and permitting liquid iron to be tapped from the bottom of the furnace with the slag as pig iron. Wrought iron was produced from the pig by puddling or finery in an oxidising furnace. The quantity and uniformity of iron produced by hand puddling was limited but mechanisation reduced quality which relied on the skill of the puddler. Fuel use changed in the 18th century from charcoal to coke. Ore type was variable by region and over time with depletion of deposits. Eventually, invention of the Bessemer Converter in the later 19th century producing mild steel at a lower cost led to its replacement of wrought iron by the 20th century.

The picture of wrought iron production is of temporal and geographic diversity of methods, batch processes and influence of individual operators, a range of ores and changing fuel. A heterogeneous material results with composition varying:

- microscopically between bulk of iron and slag inclusions and within both;
- across objects and structures forged from multiple blooms or by joining sections;
- over time with changing furnace technology and fuel type;
- regionally with ore.

It was not until 1910 that there was any regulation of production when British Standard 51 was introduced to test and certify new wrought iron for use in railways and 1939 that this was extended to cover wrought iron for general engineering purposes (British Standards Institute 1910; British Standards Institute 1939). The previous variability in composition greatly affected the properties and quality of the material.

1.1.2 Composition and properties

Wrought iron is essentially a composite material of ferrite, small amounts of carbon and entrapped slag stringers (Scott and Eggert 2009, 165). Slag can form up to 3wt% of the total mass of wrought iron with thickness of inclusions ranging from microscopic to 3mm (O'Sullivan and Swailes 2009, 261). Figure 1.1 is a Nital etched polished section of wrought iron showing the characteristic variable grain sizes and two phase slag (typically globular wüstite, FeO, dendrites in a glassy siliceous matrix) (Scott 1991, 89). A representative elemental analysis range for wrought iron is given Table 1.1.

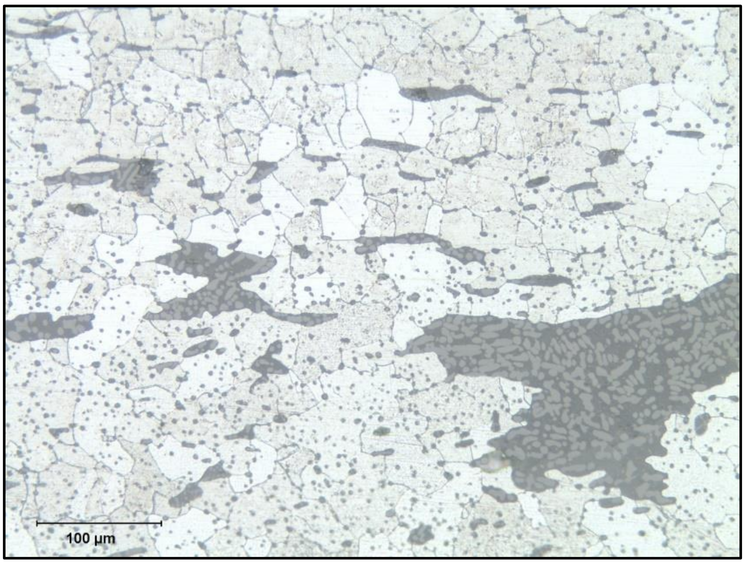


Figure 1.1 *Polished section of railing wrought iron sample material (4.2.2) used in this study. Etch: Nital. Variable grain size and two phase (typically rounded wüstite (FeO) dendrites in a glassy matrix) slag as small particles and larger fragments are characteristic of wrought iron (Scott 1991, 89).*

Element	**Content in wrought iron (%)**
Carbon	0.02 – 0.03
Silicon	0.02 – 0.10
Sulfur	0.008 – 0.02
Manganese	0.00 – 0.02
Phosphorus	0.05 – 0.25
Slag	0.05 – 1.50
Iron	Balance

Table 1.1 *A representative analysis range of wrought iron (Higgins 1957, 36).*

Improving techniques and furnace technology increased the scope and efficiency of wrought iron production. Associated compositional changes result, for example a decrease in phosphorus content of Romano British wrought iron relative to earlier material. Phosphorus content is determined by ore and fuel, sulfur by ore (until later coal fired furnaces), and nickel and copper content by ore (Tylecote 1976, 32). Phosphorous, manganese, sulfur and silicon may indicate furnace temperatures by their degree of reduction into the iron (Starley 1999, 1128). Carbon content evidences smelting technique and influences properties; malleability and ductility are reduced by increasing carbon content (Tylecote 1976, 32; O'Sullivan and Swailes 2009, 261).

Rolling of puddled iron elongates the masses of slag in the direction of rolling and they are visible as streaks in longitudinal section and dots in transverse (Higgins 1957, 36; Greaves and Wrighton 1967, 82; O'Sullivan and Swailes 2009, 261) (Fig. 5.1 & 5.29). Amount and distribution of slag depends on extent of working during forging and influences properties of the wrought iron. Tensile strength of plate wrought iron is greater along the grain (direction of rolling) than across it and is more resistant to bending about the axis perpendicular to the grain than parallel to it (Greaves and Wrighton 1967, 83). When load is across the grain, slag filaments running perpendicular to the load path act as voids for propagation of internal cracks (O'Sullivan and Swailes 2009, 266). With slag central to mechanical properties of wrought iron, variability in its mass and distribution affects its behaviour. Within a wrought iron structure, sections will have undergone different degrees of working causing an inhomogeneity of properties across the structure. Testing of historic wrought iron properties must be on large samples relative to the slag inclusions to ensure representation of the bulk material (Hooper et al. 2003, 78).

This inherent variability in wrought iron offers challenges to conservation in predicting its corrosion behaviour and mechanical properties. A one-size-fits-all approach cannot be expected to succeed, particularly given the nature of historic wrought iron objects and structures.

1.1.3 Form and function

Early ironwork took the form of domestic and military items which become archaeological or museum objects with corrosion controllable by manipulation of the internal environment. By the 18th century wrought iron was in use for gates and railings (Tijou screens at Hampton Court Palace and the Davies Brothers' gates at Chirk Castle) (Fig. 1.2), garden ornamentation (Thomas Bakewell garden arbour) and street furniture (Hayman 2011).

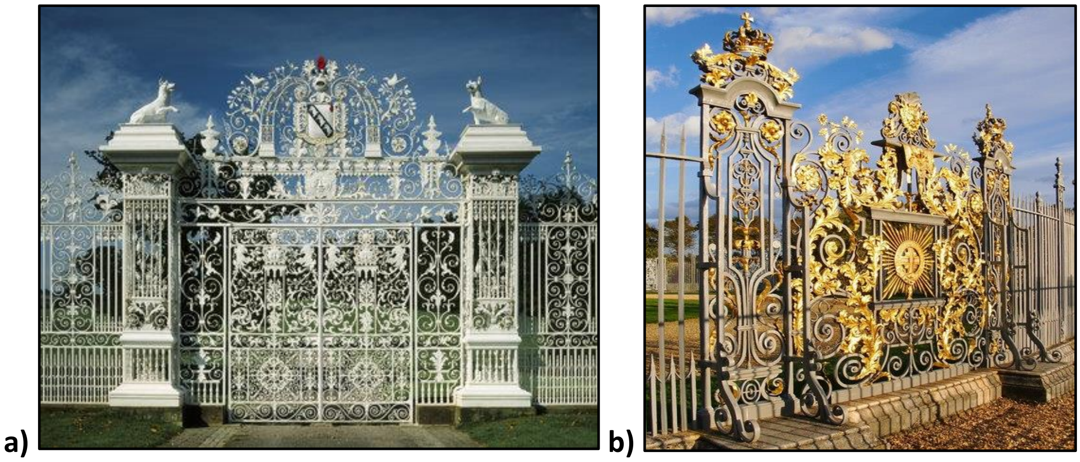


***Figure 1.2** Wrought iron gates and railings **a)** Davies Brothers gates at Chirk Castle (http://www.ntprints.com/image/374510/the-magnificent-wrought-iron-gate-at-chirk-castle) **b)** Tijou Screens at Hampton Court Palace (http://www.geograph.org.uk/photo/2657762)*

An array of historically significant industrial ironwork exists as bridges, mining and other industrial plant, equipment and infrastructure embodying industrial and technological progress, period and society (Kreislova et al. 2013, 311-314). High tensile strength allowed wrought iron plate to become the basic device of construction as riveted rolled sections could span required distances and carry sufficient loads for railway bridges, unlike cast iron (Topp 2010). Joining techniques for wrought iron included welding but also mortice and tenon joints, rivets and collars influenced by carpentry (Taylor and Suff 2010). Much industrial ironwork takes the form of trusses, tubes and piping systems which are part of larger objects or sheets (Kreislova et al. 2013, 330). 1843 saw the first extensive use of wrought iron for the hull of a ship with the launch of the ss Great Britain (Fig. 1.3) (Watkinson and Tanner 2008; Watkinson et al. 2006).

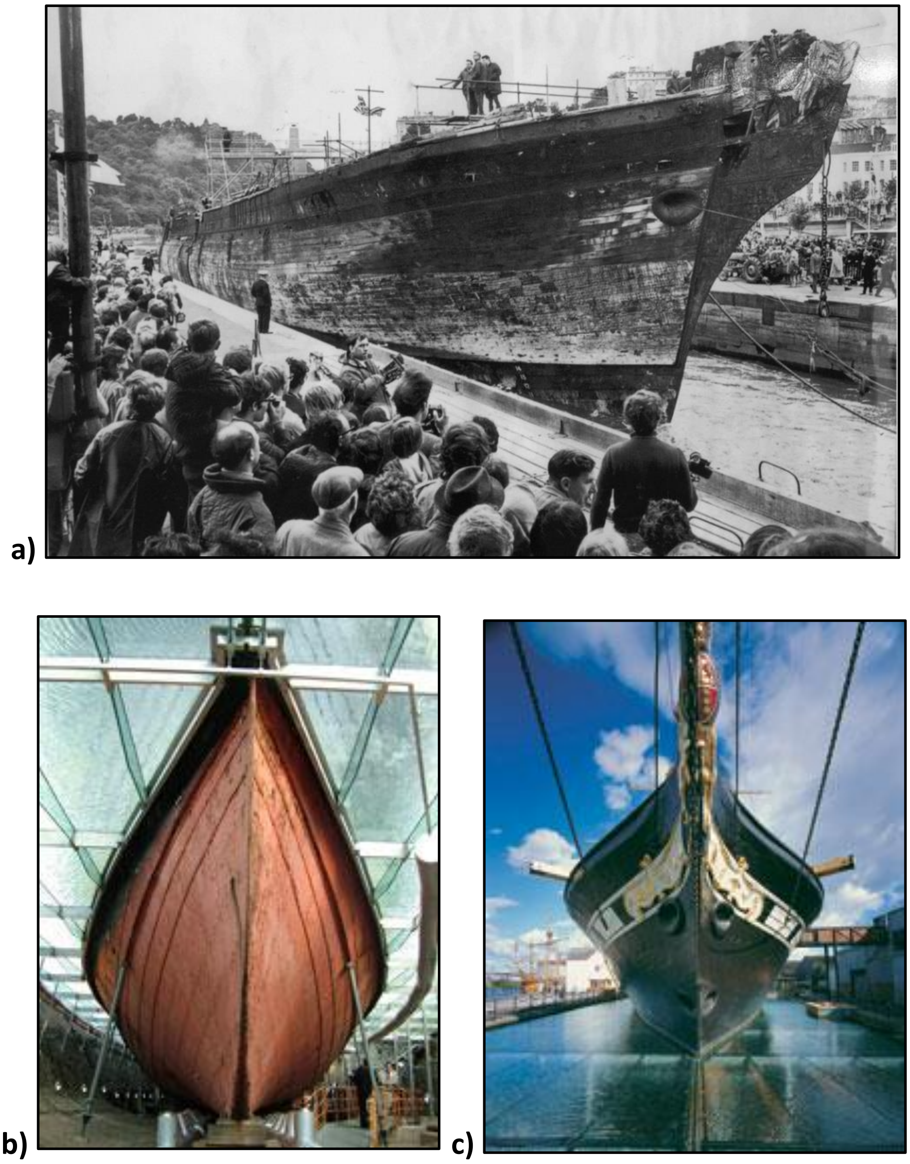


Figure 1.3 *Wrought iron ship ss Great Britain* ***a)*** *returning to its dry dock in Bristol 1970* ***b)*** *the hull in sealed dry dock with desiccation plant to control humidity* ***c)*** *epoxy resin coating to minimise atmospheric corrosion of the freeboard. Images ss Great Britain Trust.*

The diversity of wrought iron objects and structures in heritage contexts means responsibility for their preservation falls to individuals who have varying degrees of treatment experience. Objects may be in museum collections curated and conserved by specialists, items of street furniture the responsibility of local councils, gates and railings on historic properties managed by the likes of The National Trust, Cadw or Historic Scotland with or without dedicated or peripatetic conservation staff or could equally be in the private sector. Its condition may be anywhere from well-maintained with corrosion limited to closely adherent oxides overlying a substantial metal core to extremely corroded with laminating corrosion products, significant loss of section and minimal metal core remaining. The challenges in dealing with its preservation are significant. The decision-making process for individuals specifying and carrying out corrosion protection treatment of exterior historic wrought iron and the guidance available to underpin decisions are discussed in 3.4.

1.2 Research in heritage wrought iron

Heritage wrought iron may be on display or in store as part of museum collections but frequently occurs outdoors exposed to prevailing conditions. Whatever its context and despite variability of available finance, resources and expertise, management of iron objects and structures aims to reduce corrosion rates to a bare minimum for maximum longevity of object lifetimes. Achieving this requires decision-making on treatments and appropriate environments that is based on empirical evidence of resultant corrosion rates and proven success in their reduction.

Storage and display in low humidity environments has been studied extensively for objects and structures, small and large (Watkinson and Lewis 2004; Rimmer and Watkinson 2010). This research has been driven by big budget projects such as the development of an award winning, innovative conservation strategy for the ss Great Britain and by the needs of large institutions housing vast iron collections which test management protocols (Watkinson et al. 2005). In contrast, conservation of historic wrought iron exposed externally and above ground has received little attention yet it offers a significant challenge to specifiers and practitioners responsible for its survival and treatment.

Outside conservation, wrought iron has been studied by workers concerned with its metallography (Bates 1984; Blakelock et al. 2009), technology and history of production (Light 2000; Sutherland 2009; Charlton et al. 2012) or unusual examples (Kumar and Balasubramaniam 1998) and corrosion mechanisms (Neff et al. 2006; Degrigny et al. 2007; Maréchal et al. 2007; Monnier et al. 2007; Bouchar et al. 2013). Industrial and engineering research deals with atmospheric corrosion and protective coatings but focuses on modern steel substrates limiting direct applicability to heritage. There has been no holistic overview bringing these studies together and relating them to exterior historic wrought iron exposed to atmospheric conditions and requiring corrosion prevention conservation treatment. Further relating conservation products and methods and introducing empirical evidence of effectiveness of treatments whilst considering the unique nature of this conservation context and the diverse range of individuals responsible for the wellbeing of this material has never been carried out. As a result, the limited guidance available to underpin practice in this area is anecdotal and unstandardised. Recourse to British Standards is unsatisfactory as they are designed for engineering and industry and are not fit-for-purpose for heritage contexts, historic materials and related ethical concerns.

This PhD takes the approach of integrating metallurgy, corrosion theory, conservation and industrial practice and experimental study as befits a material occupying a niche position between heritage, industry and engineering. Practitioner methods for wrought iron treatment are studied to develop testing protocols. Quantitative and qualitative evidence of effectiveness of surface preparation methods and protective coatings is generated and will be used to produce guidance tailored to the needs of specifiers and practitioners directly involved in developing and implementing treatments. Focus is on delivering the required empirical data to underpin effective decision-making for heritage.

1.3 The study in context

This study has been commissioned by Historic Scotland to extend the largely qualitative testing of conservation methods previously carried out for historic cast iron. Having a rich cast and wrought iron heritage and with the traditional built environment and heritage tourism important economically (Ecorys 2013), examining treatments for traditional building materials is a strategic concern. Selection of methods for ironwork preservation is currently based on practitioner experience and anecdotal reports. Empirical evidence will allow decisions to be made with a strong underpinning rationale developed from understanding of treatment effects on materials and their long term survival prospects. Consideration of practicalities, resource implications and maintenance regimes is integral to examination of methods in this study and enriches the decision-making conversation. Results will contribute to informing future treatments specified by Historic Scotland and strengthen their position for offering evidence based advice to others in this field.

Conservation at Cardiff University has developed an international reputation for delivering the empirical evidence essential for effective management of heritage assets, particularly ferrous metals. This PhD follows successful determination of ‘safe’ relative humidity values for chloride infested wrought iron (Watkinson and Al Zahrani 2008; Watkinson and Lewis 2004; Watkinson and Lewis 2005a; Watkinson and Lewis 2005b; Watkinson and Tanner 2008) and efficiency of chloride extraction treatments for archaeological iron (Watkinson and Al Zahrani 2008; Rimmer and Watkinson 2010; Watkinson et al. 2013). Sector guidelines for the storage of archaeological iron resulted which direct practices in this area nationally and internationally (Rimmer et al. 2013). The current ferrous metals conservation research at Cardiff includes further investigation of desalination treatments for archaeological iron and study of clear coatings for armoured steels alongside this project, all of which share the focus on empirical evidence of treatment successes and generation of sector guidance for effective decision-making and management.

1.4 Aim and objectives

The study aims to perform a cost benefit analysis of corrosion prevention treatments for historic wrought iron including surface preparation methods and protective coatings systems.

This will be achieved by:

- Engagement with practitioner methods, materials and decision-making processes to tailor laboratory testing to produce fit-for-purpose, standardised test methods.
- Generation of empirical data on the impact of surface preparation methods and coating systems on high humidity corrosion rates of historic wrought iron.
- Relating practicalities to empirical data on treatment performance to underpin effective and holistic sector guidance.

1.5 Thesis structure

The breadth of this study dictates its background context and underpinning theory is equally broad and drawn from a range of disciplines. It is not the intention of the thesis to explore in great detail all aspects of atmospheric corrosion or mechanisms of protection by protective coatings. A selective approach is taken with corrosion and coatings theory being reported and discussed as relevant to the context of historic wrought iron corrosion and treatments. Chapter 2 presents an overview of the principles of corrosion and specific mechanisms of atmospheric corrosion of iron and offers an introduction to corrosion prevention by protective coatings. These background themes give the context for the conservation problem presented by wrought iron in uncontrolled exterior conditions.

Chapter 3 explores traditional and current practice in corrosion prevention for historic wrought iron. Practitioner methods of surface preparation and application of protective coatings link to theory in Chapter 2 and the critical sector problem of lack of standardised guidance and empirical evidence to direct practice is explained. This presents the context and rationale for the experimental study of surface preparation methods and protective coatings which is detailed in Chapter 4. Central to this chapter is the development of a method which not only answers the research questions proposed here but is also standardised and applicable to other studies thus encouraging further generation of empirical data. Results are offered in Chapter 5 and discussed in Chapter 6.

The discussion is intended to examine the empirical data generated and to fit that into decision-making in heritage sector treatment of wrought iron. Empirical data is balanced against practicalities in the context of specification, tendering, practice and conservation ethics. Limitations of the study and scope for further work to enhance the dataset are proposed. Conclusions are drawn in Chapter 7 regarding the insight afforded by the results of this study and the contribution it makes to developing evidence based management through data production and delivery of a standardised method which could be used in further work and by other workers to increase the breadth and depth of empirical data.

2 Corrosion Principles: Heritage wrought iron and its contexts

This chapter is intended to introduce the concepts of corrosion and corrosion prevention which dictate the problems and offer potential solutions in preservation of historic wrought iron. An overview of corrosion and coatings theory is presented followed by a discussion of the extrinsic and intrinsic factors that drive corrosion of exterior wrought iron and impact on coating performance. These are contextualised with examples of heritage objects and structures.

2.1 Principles of corrosion

2.1.1 The corrosion process

Metal extraction involves large amounts of energy to separate the metal from its compounds within its ore. This elevates it to a higher energy state where it is thermodynamically unstable relative to its lowest energy state, which is as an ion combined with other elements (Trethewey and Chamberlain 1995, 69). Therefore the natural tendency is for metals to oxidise, combining primarily with oxygen and elements such as sulfur and carbon. Metallic corrosion occurs either as an electrochemical process involving water and dissolved ions (Scully 1990, 55) or as direct oxidation at high temperatures where moisture is not involved (Jones 1992, 407). Each metal has its own energy value, which is recorded in the electrochemical series as a positive or negative potential relative to the standard hydrogen electrode (SHE), with all readings taken in standard conditions of temperature, pressure and ionic concentration (Jones 1992, 41). While this offers a guide to their thermodynamic reactivity, with more negative potentials being more prone to oxidation, it does not take into account kinetic factors such as solubility, conductivity and the coherence of corrosion layers they develop in their service life.

Since the research reported here is based on wrought iron this is used to exemplify the electrolytic corrosion process (Fig. 2.1). Electrolytic corrosion is a redox reaction.

Solid phase contact and electronic conductivity must occur between dissimilar metals or areas of differing energy within the same metal to create a potential difference that transfers electrons from high to low energy areas (Trethewey and Chamberlain 1995, 41). Electrons are generated by oxidation of the metal to its ionic form at an anode and these are passed in the solid phase to a cathode, where they are consumed by reduction reactions. Charge balance between anode and cathode is completed by movement of ions in the aqueous phase.

The mix and concentration of ions in solution, pH and ambient gasses capable of dissolving in the electrolyte dictate the range of corrosion products that can form. These may be solids formed by precipitation or dissolved ionic species according to the thermodynamic stability fields of the products. Corrosion products can have a major impact on corrosion rate due to kinetic factors. Electrolytic corrosion is an all or nothing process; if one part of the reaction sequence is prevented the whole reaction ceases and this forms the basis of methodologies for corrosion prevention. Thus the role of coatings is to block access of oxygen and moisture to the metal surface and offer electrical insulation.

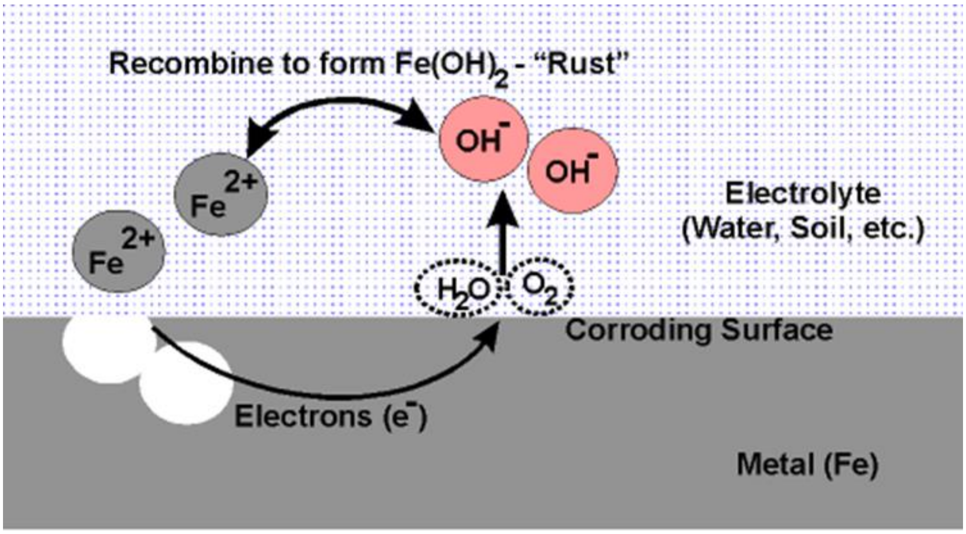


***Figure 2.1** Electrolytic corrosion of iron.*

2.1.2 Corrosion of iron: an overview

For iron corrosion the anode reaction produces ferrous ions, releasing two electrons [1] and occurs readily with a standard electrode potential of -0.44V (Cornell and Schwertmann 2003, 491). In aerated aqueous solutions over pH 4 to 14 the favoured cathode reaction is the reduction of oxygen to produce hydroxyl ions [2] (Stratmann and Müller 1994; Jones 1992, 7; Scully 1990, 55).

Anode $Fe \rightarrow Fe^{2+} + 2e$ [1]

Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ [2]

The ferrous and hydroxyl ions combine to form ferrous hydroxide [3] and further oxidation will lead to the production of iron oxides. These have many forms and the particular oxide produced will depend on factors such as oxygen availability, pH and the range and concentration of dissolved ions in the electrolyte (Cornell and Schwertmann 2003). This influences ongoing corrosion rate as thickness, coherence, conductivity and density of corrosion products will influence oxygen access to the metal surface and movement of ions away from cathode and anode sites. Coherent layers can lead to insufficient oxygen ingress to support cathode reactions, charge build up that reduces corrosion rate and the production of passivating layers on the surface of the iron.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ [3]

The abundance of hydrogen ions at acidic pH values makes the reduction of H^+ to hydrogen gas possible [4] (Trethewey and Chamberlain 1995, 76). Reaction [2] continues in such conditions but as oxygen concentration in the electrolyte falls the high H^+ concentration allows reaction [4] to dominate as the main reaction below pH 4 (Stratmann and Müller 1994; Scully 1990, 55). However, in most atmospheric environments reduction of oxygen is the favoured cathode reaction unless electrolytes are stagnant, oxygen access is restricted and hydrolysis of cations lowers pH.

$2H^+ + 2e \rightarrow H_2$ [4]

In terms of corrosion product build up delivering passivity to the metal, predominance of reaction [4] is particularly damaging as many oxides are soluble at low pH values (Cornell and Schwertmann 2003). This prevents the formation of any passive oxide layer. Reduction to hydrogen must occur on a bare metal surface and will cease if a coherent non-conducting oxide layer forms and prevents this access.

Additionally, the hydrolysis of Fe^{2+} ions [5] can lead to low pH values in the vicinity of the anode, which will hinder the precipitation of solid corrosion products. Hydrolysis reactions involving more oxidised Fe^{3+} are possible and these will also lower pH. In pitting of stainless steel in 0.5M NaCl a pH of 4.8 has been recorded at anodic sites (Suzuki et al. 1983) and, considering equilibrium constants, Turgoose showed this was due to Fe^{2+} hydrolysis (Turgoose 1982a). Potential, diffusion within electrolytes, delocalisation and precipitation of Fe^{2+} will influence how low pH values can become, with stagnant environments inside corrosion pits offering ideal conditions for low pH values.

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+ \qquad [5]$$

Corrosion rate will relate to the nature, integrity and morphology of the corrosion layers produced on surfaces and whether they exist as solids, since this influences transfer of reactants to anodes sited on the metal surface and the movement of ions from anodes to cathodes. Voluminous corrosion products will lack coherence and be more permeable to gases and vapours than dense more evenly formed layers that offer better oxygen and moisture ingress. Examining potential/pH diagrams reveals that for many metals their corrosion products are soluble at low pH and therefore only ionic species are the stable phases and no solid corrosion layers form to hinder corrosion (Krauskopf 1982, 204). Kinetic properties of corrosion products influence corrosion, as conducting corrosion products such as Fe_3O_4 can establish cathodes remotely from the metal surface and support corrosion (Cornell and Schwertmann 2003, 115).

Corrosion may take the form of uniform or general corrosion, where a flux of energy over the metal surface creates constantly changing anodes and cathodes, delivering an even loss of metal over the entire surface (Jones 1992, 11), or fixed cathodes that produce local corrosion, which has several forms including pitting (Trethewey and Chamberlain 1995, 168) and crevice corrosion (Jones 1992, 12). Galvanic corrosion is a specific form of corrosion where the energy between two differing metals drives the process and the greater the potential difference between them the faster the corrosion rate (Trethewey and Chamberlain 1995, 130; de Rooij 1989). The more electronegative metal acts as the anode and is oxidised, while the less energetic metal receives electrons and acts as the cathode which protects it from corrosion. Galvanic corrosion appears to be ongoing and destructive but it ceases when a build-up of insoluble non-conducting corrosion products is formed between the two metals, as this prevents solid phase electron transfer. Both metals then corrode individually, provided the conditions for electrolytic corrosion exist. There are multiple causes of general and local corrosion including intrinsic factors such as alloying and inhomogeneity, as well as external factors such as oxygen concentration within electrolytes, these and other factors are addressed later in this chapter.

Atmospheric corrosion of clean metal surfaces is initially fast due to access of oxygen and moisture to the metal surface feeding electrolytic corrosion but later slows if insoluble corrosion products form that hinder access to the metal surface creating passivity (Kucera and Mattsson 1987). Products from reactions [1] and [2] can react with each other and other ambient ions to produce corrosion products, however corrosion mechanisms are more complex than would appear.

The mechanism of rusting in the atmosphere caused by rain events is different to that occurring in bulk aqueous systems, due to its three phase system (Dillmann et al. 2004; Hoerlé et al. 2004). This involves a range of steps from initial reduction of corrosion products through the anodic dissolution of iron to reoxidation of the reduced iron species (Fig. 2.2) (Dillmann et al. 2004; Hoerlé et al. 2004; Maréchal et al. 2007).

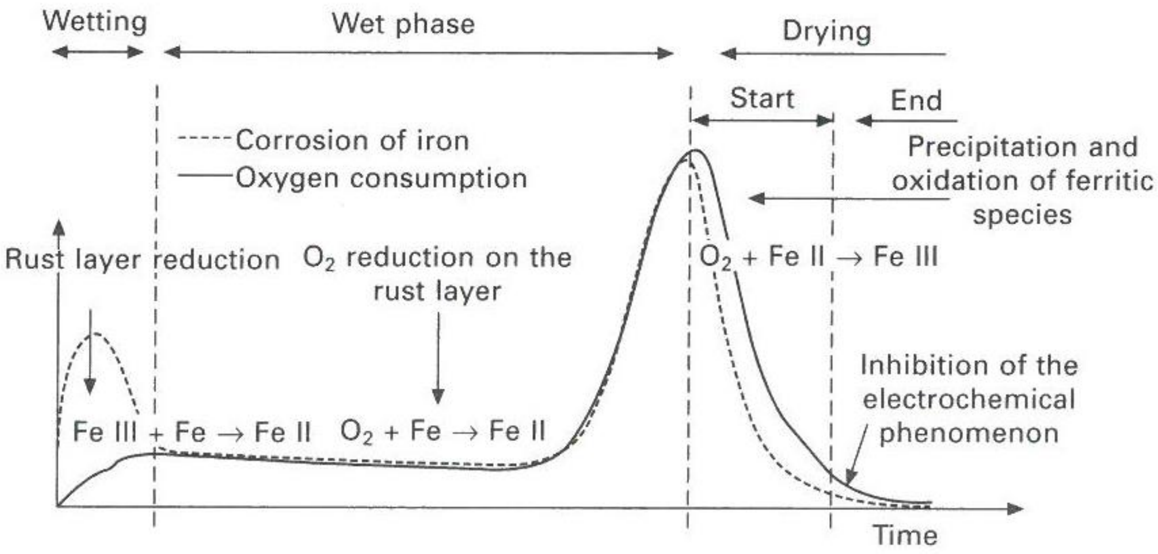


***Figure 2.2** Corrosion process during wet/dry cycle phases (Maréchal et al. 2007).*

In the wetting phase anodic dissolution of iron is balanced by reduction of ferric species to less oxidised phases such as Fe_3O_4 (magnetite $Fe_2O_3.FeO$) and little oxygen is consumed, as evidenced by the higher consumption of iron as compared to oxygen in terms of balance between anode reaction [1] and cathode reaction [2] (Stratmann and Streckel 1990). Once ferric reduction is complete, oxygen reduction becomes the cathode reaction during the wet phase and balances iron oxidation. Finally, during the drying phase, oxygen oxidises the reduced species formed in the first phase and any new oxidisable species produced by corrosion to produce FeOOH. Drying eventually stops corrosion. Reduction of γFeOOH in the wetting phase depends on potential; Fe_3O_4 is formed from αFeOOH at potentials lower than -0.9V (SHE) and γFeOOH at -0.5V (SHE) (Dunnwald and Otto 1989). The reduction of γFeOOH begins at the metal surface and progresses outwards along pore walls (Cox and Lyon 1994).

Atmospheric corrosion typically produces a rust layer that contains some Fe_3O_4 within its inner layer and the more oxidised FeOOH ($Fe_2O_3.2H_2O$) polymorphs form its outer layer, with spaces within the magnetite layer being 'plugged' by the formation of corrosion products produced by water and oxygen ingress through cracked corrosion layers (Jones 1992, 404). This profile is almost universally observed and fits a more detailed description of a dense inner layer of Fe_3O_4, amorphous

FeOOH overlaid by a looser crystalline layer of $\alpha FeOOH$ (goethite), $\gamma FeOOH$ (lepidocrocite) and γFe_2O_3 (maghemeite) (Leygraf and Graedel 2000, 285). Overall, it also aligns well with the mechanism occurring during wetting and drying cycles described by Hoerlé et al. (2004). Green rusts ($[Fe_2^{II}Fe^{III}O_X(OH)_y]^{(7-2x-y)+}$ and $[Fe_2^{II}Fe^{III}O_X(OH)_y]^{(5-2x-y)+}$) also occur within corrosion layers but these Fe(II) – Fe(III) compounds are unstable and are intermediates that transform to more oxidised species when exposed to oxygen (Refait et al. 1998; Leygraf and Graedel 2000, 284; Cornell and Schwertmann 2003). Characterisation of medieval wrought iron corrosion products on wrought iron bars corroded inside Amiens cathedral has identified ferrihydrite ($5Fe_2O_39H_2O$; nominal formula) and feroxyhydrite ($\delta FeOOH$), which are less crystallized phases (Monnier et al. 2007). Many other corrosion products can occur but this overview records the most commonly occurring products. Specific environments such as sulphate and chloride rich contexts will influence corrosion product formation and are discussed later.

While a simple stoichiometric equation for rusting can be offered [6] not all oxygen consumed can be directly linked to loss of iron as the wet/dry reaction phases involve reduction of oxides and their later re-oxidation. However, given that the reactions occurring on rusting iron surfaces will follow similar reaction routes, the principle of using oxygen consumption for quantitative comparisons between corrosion rates is viable. This is described in 4.1.3, 4.2.5 and 4.2.6. Corrosion mechanisms and routes are examined in more detail in section 2.3.

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH \qquad [6]$$

2.2 Corrosion prevention by protective coatings

Reducing the rate of atmospheric corrosion of metals is achievable by modifying the environment to make it less corrosive, by exploiting electrochemical principles to suppress anodic or cathodic reactions or by separating the metal from the corrosive environment and introducing a large resistance to impede ion transport between anode and cathode (Scully 1990, 130; Mayne 1954, 286). It is clear from practitioner guidance and feedback that application of organic coatings, effectively separating the wrought iron from its exposure environment and exploiting electrochemical principles, is the most common approach.

Protective coatings are a complex combination of materials. Coating systems are formed of one or more layers (coats): the primer is applied to bare metal; the last coat is the finish or topcoat; any coats applied between are intermediate or build coats (Trethewey and Chamberlain 1995, 304).

Component	**Purpose**
Vehicle	Liquid giving fluidity during application and drying or curing to a solid film (see *Binder*) by evaporation of solvent, chemical change (e.g. oxidation) or polymerisation of vehicle and curing agent (two-pack coatings).
Pigment	Solid particles suspended in the vehicle. They may inhibit corrosion or corrode in preference to the substrate metal when in primers. In topcoats inert pigments lengthen diffusion pathways for oxygen/water to delay corrosion and slow reaction rates.
Additives/fillers	Accelerate drying/curing of the coating or impart desirable properties to the paint film.
Binder	Solid portion of the vehicle once dried/cured. Holds pigments, keys paint film to the substrate and functions as a barrier to oxygen, water and aggressive ions.

***Table 2.1** Components of paint coatings (Trethewey and Chamberlain 1995, 304-305).*

2.2.1 Mechanisms of protection

Corrosion prevention is one of the least well understood and most unpredictable properties of organic coatings but there are three main mechanisms by which it occurs (Bierwagen 1996, 44):

i) Barrier protection (transport of aggressive species to the metal surface is impeded by coatings with low permeability for gases, liquids and ions);

ii) Cathodic/sacrificial protection (sacrificial corrosion of an electrochemically less stable metal);

iii) Inhibitive/passivation protection (by a chemical conversion layer or inhibitive pigments within the coating).

Barrier coatings typically contain inert pigment (titanium dioxide, micaceous iron oxide or glass flakes) at lower pigment volume concentrations which result in dense, cohesive coatings displaying very low permeability to aggressive species (Hare 1979). It has long been recognised (Bacon et al. 1948; Kittelberger and Elm 1952; Dickie and Smith 1980; Thomas 1991) that the mechanism of protection by barrier coatings is via ionic impermeability rather than inhibition of moisture permeation. Common electrolyte ions are Cl^-, SO_4^{2-} and a mixture of cations such as Na^+, K^+, NH_4^+ and Ca^{2+} (Bierwagen and Huovinen 2010, 2647). Ionic impermeability ensures moisture at the metal surface has a high electrical resistance to minimise corrosion (Sørensen et al. 2009, 142). A typical barrier coating is a cross-linked epoxy matrix with aromatic groups forming an effective barrier to water, oxygen and ions and strong adhesion to the metal substrate promoted by many secondary hydroxyl groups (Rouw 1998, 181). In the majority of coating systems the topcoat is the layer whose primary function is to act as a barrier and the best performers in this role are hydrophobic and resistant to photooxidation (Bierwagen and Huovinen 2010, 2467-2468).

Sacrificial coatings are applied as primers. The sacrificial, more electrochemically active metal must be in electrical contact with the substrate. Zinc-rich primers offer sacrificial protection as anodic zinc will corrode in preference to cathodic iron as long as the system is conductive and sufficient zinc remains within the primer layer (Sørensen et al. 2009, 143). Penetration of water through the binder corrodes zinc to zinc hydroxide which further reacts with carbon dioxide to form zinc carbonate, filling pores in the coating and producing an impervious, compact and adherent protective layer (Kalendová et al. 2015; Trethewey and Chamberlain 1995, 305). If the primer layer is damaged, zinc corrosion products seal the pores between zinc particles, the system becomes electrically non-conductive and the corrosion products act as a barrier (Feliu et al. 1989a; Feliu et al. 1989b). Adhesive and cohesive strength of zinc-rich primers may be reduced by high volume concentrations of zinc pigment, and consequently lower percentages of binder, required to provide electrical conductivity (Kalendová et al. 2015; Greenfield and Scantlebury 2000).

Inhibitive coatings applied as primers passivate the substrate and build up a protective layer of insoluble metallic complexes which are a barrier to transport of aggressive species to the substrate (Sørensen et al. 2009, 144). Inhibitive pigments are inorganic salts (e.g. phosphates, chromates, molybdates, nitrates, borates and silicates) which are slightly soluble and carried to the substrate surface by permeating water where they react with the metal to form a passivating product which inhibits corrosion (Rammelt and Reinhart 1994, 304). Efficiency of inhibitive pigments depends on barrier properties of the coating; a degree of coating permeability triggers the effects of inhibitive pigments whereas with low permeability coatings barrier pigment effects will be predominant (Liu 1998, 576).

Coatings are frequently applied as systems. Careful selection of properties for each coating within the system maximises corrosion prevention performance. Hydrophobicity and UV resistance are desirable for topcoats, high cross-link density and adhesion to substrate and each other for intermediate/build coats and primers (Bierwagen 1996, 45).

2.2.2 Factors affecting coating performance and failure

Protective coatings fail when they no longer prevent corrosion of the coated substrate, when coating damage exposes substrates to uninhibited corrosion and when coating appearance is degraded to an unsatisfactory level by corrosion and weathering (Bierwagen 1996, 44). A failure of the coating will concentrate corrosion at that point, set up differential aeration effects beneath the paint film and further exacerbate corrosion (Trethewey and Chamberlain 1995, 307).

The main features necessary for successful protective coating are (Bierwagen 1996, 45; Sørensen et al. 2009, 137; Bierwagen and Huovinen 2010, 2646):

- Wet/dry adhesion which maintains the coating contact with the substrate and prevents damage by osmosis;
- Low ion (Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Ca^{2+}), water and oxygen permeability;

- Low conductivity preventing flow of current in local corrosion cells and ion and electron motion in the film;
- Stability of the polymer within the environment (hydrolysis, UV radiation, extremes of temperature);
- Strong absorption of coating polymer/substrate interface and good wetting of the substrate surface by the coating;
- Pigmentation for barrier and sacrificial protection mechanisms;
- Flexibility and toughness to withstand impact and cracking;
- Maintenance of appearance under stress, swelling, mechanical forces and weathering.

The range of factors affecting protective coating performance is vast and includes the composition of the coating (binders, pigments, solvents, extenders and additives), substrate types, substrate pretreatment or preparation level, curing parameters, coating thickness, adhesion of the coating to the substrate surface and various environmental factors (Sørensen et al. 2009, 137). Almost all paint media exhibit a degree of permeability to water and oxygen but the introduction of solid pigment and filler lengthens the diffusion pathway and makes this more convoluted (Ross 1977, 28). Increasing thickness of barrier coatings has been shown to reduce the delamination of defect free and intentionally damaged coatings on hot rolled steel in long term exposure tests whereas extent of surface preparation was found to have a surprisingly limited effect (Keane et al. 1969, 372; Steinsmo and Skari 1994, 934) despite assertions to the contrary (British Standards Institute 2007; Leighs 2008a; Ross 1977, 29). Pinholes in a coating (holidays) are particularly problematic as the coated surface presents a large cathode to a small anode (exposed substrate at the holiday) causing high corrosion rates (Trethewey and Chamberlain 1995, 308). Adhesion is a key attribute for successful performance of a protective coating and can be maximised by surface preparation with clean metal surfaces or metal oxides ideal for wetting due to their high surface energies (Bierwagen and Huovinen 2010, 2655).

Environmental conditions during application affect coating success. Moisture and low temperatures interfere with adhesion and completeness of cover and moisture under the coating initiates corrosion (Ross 1977, 31). Where coating/substrate adhesion is poor, salt solutions can form between water diffusing through the coating and soluble corrosion products or compounds from the coating; subsequent osmotic pressure drives faster water diffusion and causes blistering and delamination with pressure rupturing the substrate/coating bond (Fig. 2.3 and 2.4.) (Trethewey and Chamberlain 1995, 321; Greenfield and Scantlebury 2000).

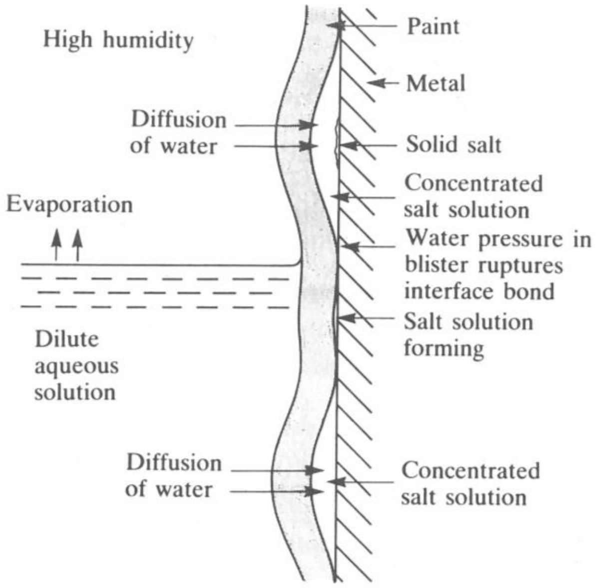
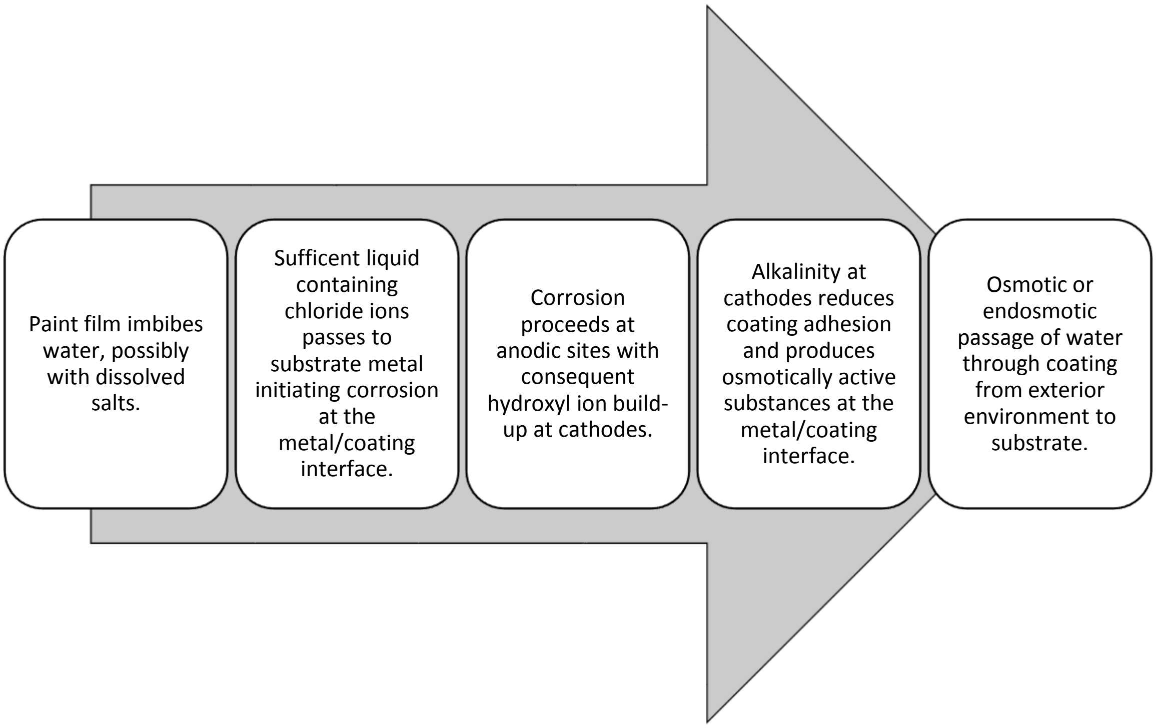


Figure 2.3 *Development of blisters in poorly adherent paint films owing to osmotic pressure (after Trethewey and Chamberlain 1995, 321).*



Paint film imbibes water, possibly with dissolved salts.

Sufficent liquid containing chloride ions passes to substrate metal initiating corrosion at the metal/coating interface.

Corrosion proceeds at anodic sites with consequent hydroxyl ion build-up at cathodes.

Alkalinity at cathodes reduces coating adhesion and produces osmotically active substances at the metal/coating interface.

Osmotic or endosmotic passage of water through coating from exterior environment to substrate.

Figure 2.4 *Suggested sequence of blister formation (Greenfield and Scantlebury 2000).*

Small failures in coatings may lead to exponential corrosion rates. A small blister in a coating or corrosion at a pinhole holiday causes a small area of coating failure which allows further ingress of oxygen, water and ions. A small anode and large cathode leads to aggressive corrosion, further spalling of paint layers, ingress of corrosive species, undermining of coatings and exposure of more substrate material for corrosion.

The effects of coating failure are seen clearly in Figure 2.5. Blistering, disbondment and lifting of coating layers has opened channels for the ingress of water, oxygen and aggressive ions. The effects of the coating delamination and exposure of the underlying substrate to uncontrolled atmospheric corrosion can be seen. Laminations of corrosion products open yet more channels for ingress of corrosion accelerants and this further corrosion results in devastating loss of metal section. Techniques preparing the surface of these gates for recoating will remove loose corrosion products and the extent of loss of original material will become clear.

***Figure 2.5** Wrought iron gates at the Palace of Holyroodhouse showing coating failure and laminating corrosion of underlying substrate.*

2.3 Corrosion variables

The interdependent nature of the processes involved in electrochemical corrosion mean that if one part of the reaction ceases the whole process stops; if there is no water there cannot be movement of ions in the aqueous phase; loss of solid phase electron conducting contact between anode and cathode prevents transfer of electrons. Ambient environment controls availability of the aqueous phase and factors such as the build-up of non-conducting corrosion products between anode and cathode control electron movement. The variables that facilitate, drive and control corrosion are reviewed to offer an overview of corrosion, how coatings can prevent this and how they begin to fail in this task.

2.3.1 Water

Moisture in the atmosphere is measured as relative humidity (RH), which is the ratio of moisture in the atmosphere to the amount of water it can hold before dew point occurs (Thomson 1986, 68). This is a temperature dependent function; warmer air can hold more moisture before dew point. At sufficiently high RH, termed critical RH, enough moisture is adsorbed onto a metal surface to provide a continuous layer that can support electrolytic corrosion with early work determining this to be in the region of 60%-70% RH (Vernon 1935).

Electrolytes are formed by soluble ionic contaminants on the metal surface or gaseous pollutants that dissolve in the film. Generally corrosion is considered to be negligible where monolayers are only 1 to 2 layers thick but adsorbed water films are 2 to 5 layers thick at 60% RH and corrosion begins to escalate and becomes significant at 80% RH, where the layers are 6 to 10 layers thick (Leygraf and Graedel 2000, 11; de Rooij 1989). At the critical humidity of 60% RH, water layers are likely to be clustered rather than continuous, which will influence the location of corrosion (Leygraf and Graedel 2000, 283). Water layers begin to form on polished metal surfaces around 55% RH (Garverick 1994, 5). Capillary condensation has a part to play in corrosion. Small capillaries of 1.5nm will condense water at 50% RH (Garverick 1994). Capillary condensation occurs in pores at a vapour pressure below 100% RH and occurs for water when capillaries approach 10^{-5} cm (Bikerman 1970, 309).

Consequently, corrosion product layers and dust particles can influence the development of water films on metals and lower the critical humidity for corrosion to commence. This could be particularly influential for corroded surfaces beneath failed paint films if capillary size within corrosion layers is small and soluble ions, hygroscopic salts and hydrated oxides are present. Corrosion couples between differing metals vary considerably according to RH; Cu/Fe couples (μAcm^{-2}) are six times greater at 100% RH as compared to 75% (de Rooij 1989). Time of wetness on metal surfaces has long been known to influence occurrence of corrosion (Vernon 1931).

If corrosion is to occur in adsorbed water layers dissolved salts are necessary to form electrolytes. Uncontaminated surfaces of shiny clean iron were found not to corrode even at 95% RH (Cai and Lyon 2005). A lower RH corrosion threshold value can be achieved in the presence of hygroscopic soluble salts on the metal surface, as they attract water to support electrolytic corrosion and at higher RH can deliquesce to provide strong electrolytes (Chandler 1966). Sodium chloride (Evans and Taylor 1974) and ferrous chloride (Turgoose 1982b) are two typical salts with the ability to lower the critical RH for corrosion. Solids such as carbon and ash can contain impurities such as sulfur and also increase the thickness of water layers and promote corrosion at lower RH values than might be expected (Scully 1990, 103). Chandler (1966) found that marked corrosion of steel occurred at 52% RH in the presence of chlorides or sulphates but was inappreciable below 42% RH, with concentration of dissolved ions determining the rate of corrosion rather than the amount of water uptake by the metal. This is below the accepted 60% critical humidity for corrosion of ferrous metals. Clearly, both RH and dissolved salts are important factors when considering the corrosion of metals.

2.3.2 Climate

Climate has a strong part to play in any corrosion cycle for iron or any other metal (Sereda 1974; Hayrie 1982); outdoors by direct action and indoors by influencing temperature and RH. Annual humidity patterns, location, temperature and pollution all play a part in the corrosion process and this is reflected in the choice of test site location across the world and the data sets produced at them (Hudson and Stanners

1953). Rain events produce wetting and drying cycles on the metal surface. These involve; an initial wetting phase forming a thin water film quickly followed by a saturation stage that supports a thicker film of water, which remains in place during the rain event and shortly after, then finally a drying phase with a thinning water film until it finally disappears (Hoerlé et al. 2004). Corrosion is fastest in the drying cycle, as the surface of the metal retains a thin water layer for some time and this supports the ready solvation of atmospheric oxygen and its diffusion through the layer to cathodes [2] (Leygraf and Graedel 2000, 13). In contrast, during the saturation phase the diffusion path for oxygen is longer due to the thick continuous water films and will affect corrosion rate (Leygraf and Graedel 2000, 286). The impact of climate on corrosion is clear, as many short rain showers with high humidity, low wind and limited sun will produce multiple drying cycles with slow drying that prolongs the aggressive final drying phase. Temperature mostly influences corrosion by its impact on RH values and thus availability of water (Sereda 1974).

Pollutants and contaminants can play an important role in the corrosivity of rain. Corrosion of the cables of the Williamsburg Bridge in New York City was credited to the impact of acid rain that was then prevalent in the New York atmosphere and to chloride originating from the river and de-icing salts thrown into the air by vehicular traffic (Eiselstein and Caliguri 1988). Additionally, intrinsic factors were also contributors, as the graphite contained in a slushing oil intended to protect the cables of the bridge was cathodic to the steel cable and offered a vast reaction area leading to local corrosion where the coating failed to cover the cable. This integrated attack on the metal reveals the complexity of predicting corrosion as climate, location, function, coating choice and contractor standards all influenced the corrosion pattern and rate. Similarly, rusting steels designed to develop protective rust coatings performed well in dry environments and in even wet/dry cycles but in stagnant wet conditions the formation of non-protective rust layers allowed high humidity, condensation and chloride contaminants to develop severe corrosion beneath them (Raman 1988).

2.3.3 **Oxygen**

Oxygen solubility and its diffusion to cathode sites is important in controlling rate of reaction. Solubility of oxygen in water at atmospheric pressure and 25°C is 2 x 10^{-4} mol l^{-1} in equilibrium with p_{O2} of 0.2 atm^{-1} (Stratmann and Müller 1994), which decreases with increasing temperature until freezing prevents corrosion, as there is no electrolyte. A strong electrolyte may enable corrosion to occur at low temperatures by its 'de-icing' effect of the dissolved salts lowering the freezing point of water. The porosity of corrosion product layers or protective coatings can be influenced by saturation with water, as this reduces the diffusion rate of oxygen to anode sites on the metal surface and likely favours the formation of larger quantities of less oxidised corrosion products such as Fe_3O_4.

Consequently, extended rain events may not be as negative as might be expected. As well as fewer drying cycles the micro-pores within coatings will be saturated with water and oxygen has to both dissolve and diffuse within this system, whereas dry coatings allow for better gas and vapour permeation and multiple short rain events offer scope for wet/drying cycles that are aggressive. High humidity may also lead to pores being saturated by capillary condensation. A worst case scenario is likely the retention of moisture beneath a dried and damaged coating, allowing easy oxygen ingress to feed the cathode reaction. Atmospheric humidity is important for the delivery of electrolyte and diurnal cycles of temperature can have a significant influence on RH and thus availability of electrolyte. Night temperatures normally raise RH and cool metal surfaces producing a microclimate in their vicinity, which may lead to condensation when dew point is reached promoting corrosion and offering media for better solvation of atmospheric gases.

2.3.3.1 *Oxygen starvation corrosion: rain and condensation*

Rain events can also lead to rapid local corrosion on iron and develop pitting (Trethewey and Chamberlain 1995, 169). This occurs by oxygen starvation occurring in the centre of a water drop created by the high surface tension of water (Fig. 2.6). Initially the spot is oxygenated throughout but the flux of energy over the metal surface under the spot leads to general corrosion and multiple cathodes rapidly deplete oxygen. Since oxygen replenishment within the water drop is from its exterior this develops an oxygen rich outer layer leaving an oxygen starved inner layer. Oxygen starvation produces an anode at the centre of the spot [1], with cathodes sited at the oxygen rich outer layer that use up oxygen before it can diffuse into the drop centre [2]. Hydrolysis reactions, such as that of Fe^{2+} at the anode [5], lead to low pH in the centre of the spot hindering formation of solid corrosion products. Migration of Fe^{2+} from the anode leads to their reaction with cathodically produced OH^- precipitating $Fe(OH)_2$ [3] in the vicinity of the cathode, further oxidation of this hydroxide produces iron oxides. This creates a ring like corrosion pattern with an anode at its centre leading to pitting corrosion, which can produce quite large and wide pits that can merge into a more general corrosion layer.

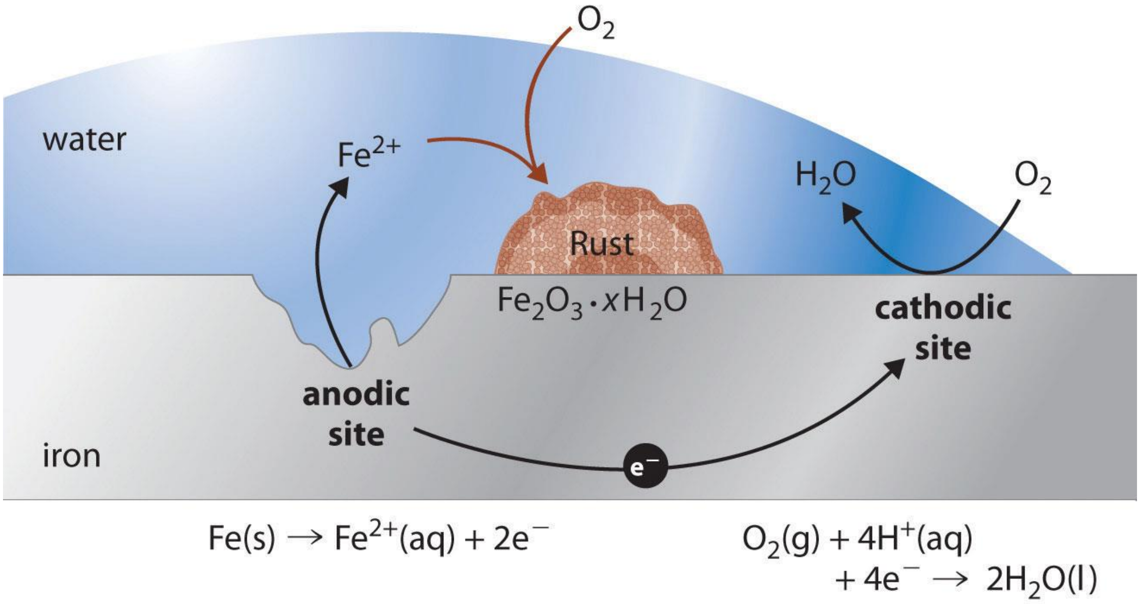


Figure 2.6 *Oxygen starvation in a water drop on the surface of iron.*

2.3.3.2 *Oxygen starvation corrosion: pitting*

Localised pitting corrosion can occur when inhomogeneity or particulate deposition creates fixed cathodes. Typically, it involves a corrosion pit containing water with a low oxygen concentration in its base and a low pH due to hydrolysis of metal ions (Galvele 1976) such as Fe^{2+} hydrolysis [5]. The low pH prevents formation of solid corrosion products and provides a large positive charge in the pit base. To counterbalance this, anions are pulled into the pit with chloride being the most common ion due to its high solubility and mobility. Electrons from the anode travel in solid phase to the pit mouth where an abundance of oxygen and availability of electrolyte creates anodes and oxygen is reduced there [2]. Migration of Fe^{2+} and $Fe(OH)^+$ towards the pit mouth oxidise to produce ferric ions [7] and [8], which can further oxidise to produce solid corrosion products whose oxidation state depends on the amount of oxygen present. In less oxidising conditions magnetite (Fe_3O_4) forms [9] and in more oxidising environments ferric oxyhydroxide (FeOOH) is the product [10]. A mixture of both at the pit mouth can be expected and this explains the appearance of rust blisters there.

$Fe^{2+} + ½O_2 + 2H^+ \rightarrow Fe^{3+} + H_2O$ [7]

$2Fe(OH)^+ + ½O_2 + 2H^+ \rightarrow 2Fe(OH)^{2+} + H_2O$ [8]

$2Fe(OH)^{2+} + Fe^{2+} + 2H_2O \rightarrow Fe_3O_4 + 6H^+$ [9]

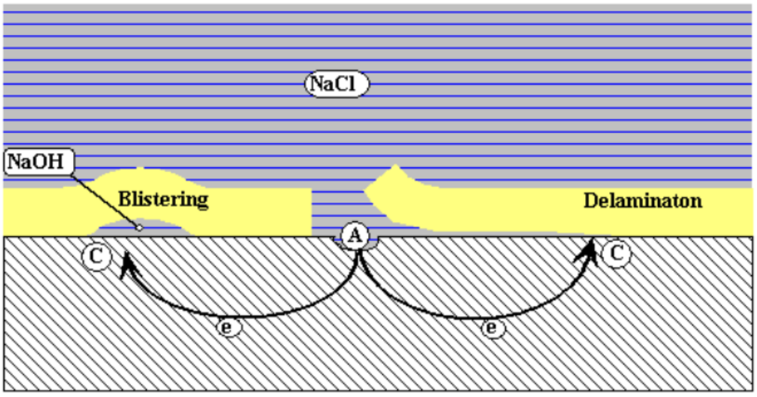
$Fe(OH)_2^+ + OH^- \rightarrow FeOOH + H_2O$ [10]

Acidity is exacerbated by the vast coastline of Britain, as chloride will be readily available in many areas of the country. This produces an Fe^{2+}/Cl^- solution with hydrolysis of Fe^{2+} [5] producing low pH values and association of H^+ with Cl^- producing HCl (Leygraf and Graedel 2000, 46) to keep corrosion products in a soluble form and maintain a low oxygen environment. The aqueous system within the pit allows Fe^{3+} to form complexes with Cl^- and mixed complexes containing Cl^- and OH^-, also drying in oxidising conditions with high Cl^- concentrations will lead to precipitation of basic oxychlorides such as β-$Fe_2(OH)_3Cl$, which is a precursor to the formation of βFeOOH (Refait and Génin 1997). Once the pit dries out corrosion ceases but can be reactivated later by water producing electrolyte and with a low pH as the ingredients for this are in place.

Pitting can occur where pinhole breaks and holidays are present in coatings and can be particularly damaging if the integrity of an iron sheet is breached by small pits penetrating its thickness. Within heritage contexts, this may or may not be a preferable form of corrosion depending on circumstance; disastrously, a functioning tank will lose its gas pressure or water tightness and be unable to fulfil its purpose, whereas localised loss of an historic paint layer by pitting may be preferred to overall loss of large areas by general corrosion, where evidence of the paint layer and surface technology or decoration would disappear entirely. Clearly, context influences the impact of the corrosion type. Further to the loss of the historical record are the aesthetic considerations for heritage objects, which can create a dichotomy of interest when the aim is to develop optimum preservation strategies.

2.3.3.3 *Coatings: cathodic disbondment and oxide lifting*

Since this dissertation is centred on surface preparation and coating performance on heritage wrought iron, cathodic disbondment and oxide lifting are important problems to consider, as they are associated with corrosion through damaged films (Jones 1992, 487) (Fig. 2.7). Cathodic disbondment involves hydroxyl ions generated by the cathode reaction [2] beneath damaged paint films being solvated and reacting with particular types of paint films, such as oils, to saponify them. This causes separation at the metal/paint interface at the macroscopic or microscopic level, which aids further oxygen and moisture ingress to support corrosion.



REACTIONS:

Anodic.........$Fe \rightarrow Fe^{++} + 2e$

$Fe^{++} + O_2 + H_2O \rightarrow Fe_xO_y + H_2O$

Cathodic......$H_2O + 1/2\ O_2 + 2e \rightarrow 2OH$

$2Na^{+} + 2OH^{-} \rightarrow 2NaOH$

Figure 2.7 *Possible consequences of coating damage (Greenfield and Scantlebury 2000).*

Oxide lifting is summarised by Jones (1992) as lifting and undercutting of paint films by compacted oxides that have dried and formed a lamellar structure. The oxide layers have a large volume. Fully oxidised iron as FeOOH forms the outer layer, while next to the metal surface ferrous species Fe^{2+} and $Fe(OH)_2$ are favoured in the low oxygen environment there, as is the formation of the partially reduced oxide magnetite (Fe_3O_4) and this is overlaid by the FeOOH forming a more oxidised outer layer due to a supply of incoming oxygen (Jones 1992, 489). These layers are formed by alternate wetting and drying cycles which impact on hydration of oxides, oxygen availability and the volume of the corrosion products. The Fe_3O_4 can be reoxidsed by ingress of oxygen to form FeOOH and the differing densities between these products means volume changes are large and frequent as a function of rain events and access to the metal surface. This is essentially the same as the atmospheric corrosion mechanism in oxygen rich environments (Dillmann et al. 2004; Hoerlé et al. 2004), where lepidocrocite reduction is the cathode reaction in the stage 1 wetting phase of the reaction process. Additionally Fe_3O_4 can act as a cathode due to its conductivity (Cornell and Schwertmann 2003, 115) and this facilitates further corrosion when the corrosion products are in a wetting cycle. In the drying phase corrosion products are deposited and these do not redissolve with a new wetting phase, thereby building lamellar corrosion which is familiar on corroded iron.

2.3.3.4 *Coatings: filiform corrosion*

Filiform corrosion is a characteristic form of corrosion occurring beneath coatings on iron but it results in only limited metal loss. The mechanism involves ingress of oxygen and moisture at a pinhole break in a coating and corrosion begins beneath, with an active head that is anodic to the metal, due to it being de-aerated by using up oxygen that cannot be easily replenished. The head produces Fe^{2+} ions [1] and this is followed by an aerated tail where the cathode reaction occurs [2], producing an inactive thin corrosion product trail as the head moves forward due to surface tension effects from the OH^- ions. A cracked and ruptured paint film results (Fig. 2.8) (Jones 1992, 226). Secondary problems arise from damaged films, as ingress of moisture and pollutants through the damaged film may set up more permanent corrosion centres that eat into the iron. The general degradation of the protective properties of the film and the corrosion that may result from this are much more problematic than the filiform corrosion itself, which is unsightly rather than severely damaging. Reducing the protective properties of the coating opens pathways for further corrosion.

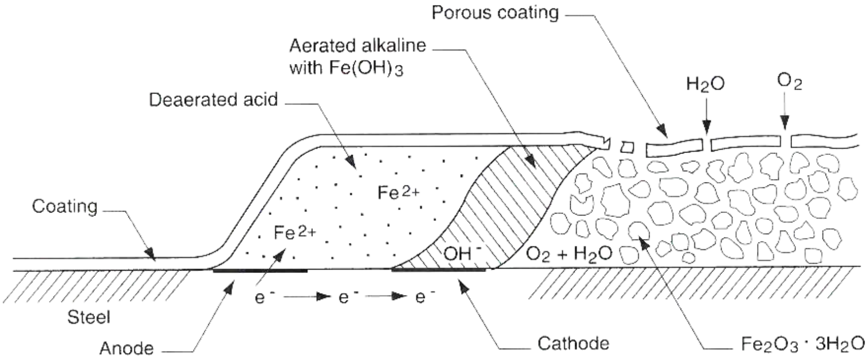


Figure 2.8 *Schematic of filiform corrosion (Jones 1992, 226).*

2.3.4 **Intrinsic factors**

The intrinsic properties of wrought iron will also influence its corrosion resistance and the nature of the corrosion that occurs. Alloying, grain structure and working of metals impact on occurrence of corrosion type and rate. Manipulation of modern ferrous alloy composition combats corrosion in alloys such as weathering steels, where intentional corrosion produces a self-healing rust layer (de Meybaum and Ayllon 1982; Knotkova-Cermakova et al. 1982). For wrought iron, alloying is less important than the quantity and distribution of heterogeneous inclusions (Dillmann et al. 2004) such as slag impurities, as the only alloying element is a small amount of carbon (0.03% maximum) and the grain structure is normally pure ferrite (Rawdon 2013, 3; Dillmann et al. 2004). Slag inclusions in ancient wrought iron are mainly faylite (Fe_2SiO_4), wüstite (FeO) and glass like inclusions (Neff et al. 2005). The amount of slag varies widely but it can act as a cathode and imperfections at slag/iron boundaries facilitate movement of ions (Neff et al. 2005). Piling during manufacture can cause lamellar corrosion that follows slag planes present from manufacturing

(Fig. 2.9) (Chilton and Evans 1955; Higgins 1957, 36; Greaves and Wrighton 1967, 82-83; O'Sullivan and Swailes 2009, 261 and 266). Both pitting and general corrosion are evident on the wrought iron plate in Figure 2.13.

Wrought iron has a reputation for good corrosion resistance and there is support for this in given contexts and relative to the orientation of corrosion in the iron (Chilton and Evans 1955). Overall general conclusions cannot be drawn on performance, as the quality of the wrought iron is crucial to its corrosion resistance. Historically it varies. At the height of wrought iron technology metal from the American Civil war ironclad *USS Monitor* was mediocre quality comprising a low carbon, high phosphorous ferrite with 4.8% silicate slag comprising phosphor and olivine, glass, wüstite and silica (Boesenberg 2006). These considerations need to be taken into account for experimental design and conclusions in this dissertation.

Wrought iron may also contain manganese, sulfur and considerable amounts of phosphorous (Rawdon 2013, 9). Manganese sulphide inclusions can occur in steels and these are strongly cathodic and will lead to local corrosion and pitting (Trethewey and Chamberlain 1995, 172). This potentially has other consequences, as acidity from hydrolysis [5] and [9] can dissolve the MnS and resulting S^{2-} and HS^{-} decrease activation polarisation on the iron, increasing its corrosion, and the low pH may support hydrogen reduction as the cathode reaction [4] with evolution of H_2 damaging the overlying oxide layer.

Figure 2.9 *Lamellar corrosion of early wrought iron railway wedge.*

2.3.5 **Pollutants and contaminants**

2.3.5.1 *Sulfur dioxide pollutants*

Sulfur dioxide can cause very significant corrosion of iron by the formation of sulfur nests (Jones 1992, 406; Leygraf and Graedel 2000, 289; Evans and Taylor 1972). These arise from the deposition of sulfur dioxide and its oxidation to sulphate and sulfuric acid lowering pH on the surface of metals. SO_2 is soluble in water with about 120g/Kg at 20°C falling to just over 50g/Kg at 40 °C and this facilitates many deposition routes. This enables SO_2 to dissolve in the damp atmosphere or adsorb onto aerosol particles allowing it to deposit in a dissolved state, often oxidised to SO_4^{2-}, also dry deposition by solvation in adsorbed water on the metal surface is possible and SO_2 reactivity with the hydroxyl radical means gas phase deposition is possible as sulfuric acid (Leygraf and Graedel 2000, 45). Water availability clearly has an important role to play in the impact of SO_2 on corrosion and correlations between SO_2 and water have been identified (Sydberger and Vannerberg 1972). Average corrosion rates for steels in the atmosphere, as a function of average SO_2 concentrations at three sites, clearly showed increasing corrosion as a function of both RH and SO_2 concentrations and it is suggested that corrosion in the presence of SO_2 should not be a problem when RH is below 30% (Hayrie and Upham 1974).

Winter is a more aggressive period for SO_2 as it is more abundant from fossil fuel use, has higher solubility at lower temperatures and winter climatic factors influence its distribution (Leygraf and Graedel 2000, 288; Mayne 1959). While sulfur was a major problem in the industrialised world, clean air policies and reduced heavy industry in Western Europe has led to reduced outputs since the late 1960's. For industrial heritage wrought iron the presence of sulfur may also be related to function, where historically equipment involved in processes such as smelting are exposed to high levels of SO_2 from the fuels involved.

The sulfuric acid produced can dissolve oxides opening up the corrosion layer to oxygen ingress and forming $FeSO_4$ which is soluble and hydrolyses to reduce pH further and open up the oxide layer more (Jones 1992, 405). Hygroscopicity of solid $FeSO_4$ and its multiple hydration states means RH corrosion thresholds for iron can fall (Rimmer and Watkinson 2010) and rust layers containing SO_4^{2-} have been shown to have reduced critical humidity for corrosion to 42% RH (Chandler 1966)

The mechanism for corrosion of iron by sulfur has been studied and an electrochemical cyclic corrosion process gradually deposits rust (Evans and Taylor 1972; Evans 1981, 109; Jones 1992, 405) [10], [11] and [12]. Fe^{2+} is generated at the anode [10] and since the pores of the corrosion layer are full of electrolyte, Fe_3O_4 is generated on the outer surface of the existing Fe_3O_4 fed by oxygen [11] (Jones 1992, 405). Cathodic reaction involves reduction of FeOOH to Fe_3O_4 [12] and this is later re-oxidised by inward migration of atmospheric oxygen [13] (Evans and Taylor 1972). Density changes will cause disruption to the corrosion product layer (FeOOH 4.26 and Fe_3O_4 5.18) (Cornell and Schwertmann 2003, 5). Some insoluble sulphate precipitates and reaction will eventually cease if there is no SO_2 replenishment. The mechanism does not require diffusion of oxygen to the metal surface and gives rise to linear corrosion rates, as diffusion through oxides and electrolyte is not necessary (Jones 1992, 400). Leygraf and Graedel (2000, 289) support this reaction process and indicate that a range of mixed oxidation state hydroxysulphates can also exist in the base of the nest.

Anode $$Fe \rightarrow Fe^{2+} + 2e \qquad [10]$$

$$3Fe^{2+} + 2OH^- + 1.5O_2 \rightarrow Fe_3O_4 + H_2O \qquad [11]$$

Cathode $$8FeOOH + Fe^{2+} + 2e \rightarrow 3Fe_3O_4 + 4H_2O \qquad [12]$$

$$3Fe_3O_4 + 0.75O_2 + 4.5H_2O \rightarrow 9FeOOH \qquad [13]$$

An acid regeneration cycle was suggested before the electrochemical model above (Schikorr 1963). This may also take place as it involves loss of sulphate from the reaction solution and this is seen to occur in small amounts as the electrochemical process continues [14].

$$2FeSO_4 + \tfrac{1}{2} O_2 + 3H_2O \rightarrow 2FeOOH + 2H_2SO_4 \qquad [14]$$

Sulfur dioxide also influences performance of protective coating systems. It has been suggested (Mayne 1959) that soluble deposits of ferrous sulphate short-circuit resistance of coatings and that given the permeability of coatings to water and oxygen the ferrous sulphate becomes oxidised and hydrolysed to voluminous corrosion products which rupture the coating film.

2.3.5.2 *Chloride*

Chloride is a major contaminant for buried archaeological wrought iron (Watkinson 2010; Turgoose 1982a) but it can also be deposited from the atmosphere. It is highly soluble and has a high transport number in water making it an ideal anion for electrolytes. It travels inwards to anodes at the metal surface to counter balance the charge produced by the Fe^{2+} ions, where its high solubility makes it a good electrolyte and corrosion rate can be expected to increase as chloride concentration rises (Chandler 1966). Additionally, depending on its concentration it can dictate corrosion product formation and produce corrosion products such as βFeOOH that promote corrosion due to the aqueous mobility of its adsorbed surface chloride (Turgoose 1982a and b; Watkinson and Lewis 2005a). Other chloride compounds can form and are precursors to the formation of βFeOOH and these include $Fe_2(OH)_3Cl$ (Neff et al. 2007). The coastal nature of the UK and location of towns and cities along the coast mean a considerable amount of heritage wrought iron will be exposed to elevated levels of chloride from marine sources. Chloride concentration falls rapidly moving inward from the coast but severe storms may take it 15km inland (Syed 2006) and lower RH facilitates further ingress of sea salt particulates from coastal areas (Gustaffson and Franzén 2000).

Hygroscopic salts can lower the corrosion threshold below the RH at which water films are deposited on metal surfaces. By attracting water to themselves they can provide water for electrolyte activity and their solubility can provide the ions for this to take place. Corrosion in the presence of sea salt is well documented (Evans and Taylor 1974) and hygroscopic salts such as magnesium chloride or corrosion products such as ferrous chloride can dramatically lower corrosion thresholds.

2.4 Corrosion products and their properties

2.4.1 The importance of corrosion products

Corrosion products and the mechanism of their formation can be wide ranging and complex, since many factors have the potential to influence which products form including; oxygen availability, moisture levels, acidity, alkalinity, temperature and availability of other ions. Their growth on iron can reduce corrosion rates to a level considered to be passive but this relies upon their continuity, morphology, porosity, solubility and whether they can conduct ions or electrons. Conducting corrosion products can support remote cathode reactions and facilitate anodic dissolution where oxygen does not access the metal surface. Pourbaix or potential/pH diagrams offer a thermodynamic guide to the formation of corrosion products by plotting their stability fields for specific concentrations of dissolved species, pH and redox potential (Fig. 2.10) (Pourbaix 1977). Introducing other ions such as chloride and elements such as sulfur or gases such as carbon dioxide to the aqueous system will influence formation of corrosion products. A brief selective review of the properties of the most common atmospheric corrosion products relevant to this study is offered.

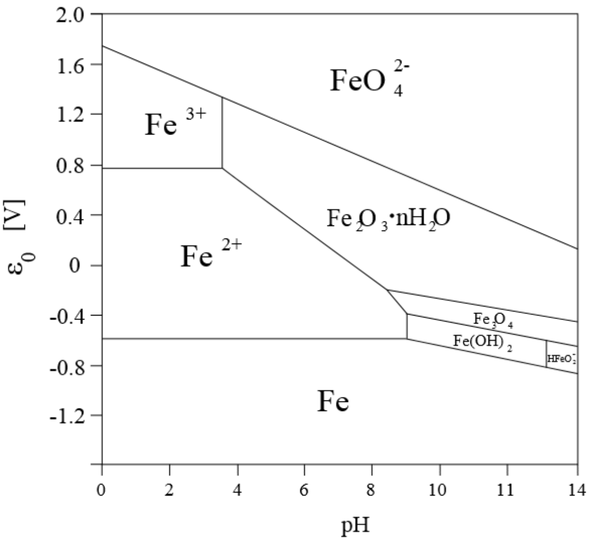


Figure 2.10 *Potential pH diagram for the iron water system at 25°C, 1 atmosphere pressure and 10^{-6} dissolved species. (Licensed under CC BY-SA 2.5 via Commons -* ***https://commons.wikimedia.org/wiki/File:Pourbaix_Diagram_of_Iron.svg#/media/File:Pourbaix_Diagram_of_Iron.svg*** *)*

2.4.2 **αFeOOH (Goethite)**

Generally the range of oxide hydroxide polymorphs have low solubility and large surface areas that make them good sorbents for gases and ions (Cornell and Schwertmann 2003, 3). αFeOOH is the most geologically stable iron oxide, is considered un-reactive and the β, γ and δ FeOOH polymorphs are unstable relative to it. It will form the greater part of the rust layer in most instances of atmospheric corrosion unless oxygen availability is limited (Hoerlé et al. 2004). It can adsorb up to 0.5% chloride onto its surface (Turgoose 1982b). It has been widely reported as occurring as a corrosion product from atmospheric corrosion (Maréchal et al. 2007; Maeda et al. 1992; Dillmann et al. 2004; Monnier et al. 2007)

2.4.3 **βFeOOH (Akaganeite)**

βFeOOH was first identified in 1935 (Weisser and Milligan 1935) as forming from conditions with high molarities of chloride and low pH either from solutions (Atkinson et al. 1977; Rémazeilles and Refait 2007) or corrosion of iron in high chloride concentrations and high RH (Turgoose 1982b). These conditions can arise on iron with significant chloride contamination, typically in pits and in the vicinity of the sea. Atmospheric drying cycles are when it is likely to form, since this is when chloride and acidity concentrate within the surface electrolyte and pits. Formation of βFeOOH from $FeCl_2$/NaOH solutions depended on $[Cl^-]/[Fe^{2+}]$ ratios and it did not occur at all for Cl^- below 1.6M but was the sole product above 3.2M, whereas high $[Cl^-]$ but low $[Fe^{2+}]$ produced only α and γFeOOH (Rémazeilles and Refait 2007). Its formation is preceded by intermediates such as $\beta\text{-}Fe_2(OH)_3Cl$ (Rémazeilles and Refait 2007; Dillmann et al. 2004) and green rusts, which is likely why low $[Fe^{2+}]$ prevents its occurrence as the necessary intermediates cannot form. This highlights the complexity of βFeOOH formation.

It has chloride occluded in its tunnel like crystal structure and adsorbed on its surface (Stahl et al. 2003), with total w/w chloride varying from as little as 0.3% to as high as 18% for βFeOOH formed in marine contexts (Childs et al. 1980; Ishikawa and Inouye 1975; Keller 1970; Watkinson and Lewis 2005a) and Thickett recorded chloride contents between 3% to 14.8% in βFeOOH naturally formed on archaeological objects post excavation (Thickett and Odlyha 2014). Recent study suggests up to 6%

chloride is occluded in tunnels and only 1% mass reduction of tunnel chloride was achieved in aqueous washing procedures, leading to the conclusion that the residual chloride posed no corrosion threat as it was effectively locked in the crystal structure (Réguer et al. 2009).

Surface adsorbed chloride is readily removed by washing (Watkinson and Lewis 2005b; North 1982) making it available to support corrosion (Turgoose 1982b). It has been shown to be hygroscopic adsorbing water onto its surface (Kaneko and Inouye 1979; Watkinson and Lewis 2005b) and corrodes iron in contact with it down to 16% RH (Watkinson and Lewis 2004) and Thickett and Odlyha (2014) detected corrosion at 13% RH. Reactions at these RH values are very slow and only begin to accelerate appreciably around 40% RH (Watkinson and Lewis 2004b). As with most electrolyte driven reactions on iron, corrosion rate begins to increase significantly around 55% - 60% RH, which is in line with critical humidity for corrosion. βFeOOH is insoluble and will remain on the metal surface but rain events can be expected to wash off adsorbed chloride. Hydrolysis of mobile surface adsorbed chloride may produce volatile HCl, as at 92% RH iron in an enclosed desiccator containing βFeOOH corroded remotely (Watkinson and Lewis 2004b).

It can be expected to occur in rust when iron is corroding in chloride rich contexts; again emphasising the importance of geography, climate and surface preparation before application of coatings. Analysis of two objects from coastal sites detected βFeOOH alongside αFeOOH and γFeOOH which are both expected as the more commonly occurring rust components in atmospheric conditions (Maeda et al. 1992). It is both electrochemically and physically dangerous, promoting oxidation of iron at low humidity and its tower-like growth causing physical damage to overlying corrosion layers and coatings. At low RH over long time periods its formation and presence under coatings could support slow corrosion that promotes coating disruption. This highlights the importance of surface preparation to remove chloride prior to coating. It has been detected in many heritage contexts; within iron bars inside Amiens cathedral (Monnier et al. 2007); on the iron hull of Brunel's *ss Great Britain* (Watkinson and Lewis 2004); and archaeological objects (Refait et al. 1992; Réguer et al. 2006).

2.4.4 γFeOOH (Lepidocrocite)

γFeOOH is a common corrosion product in rust layers and has been widely reported on outdoor iron (Graedel and Frankenthal 1990) and indoors (Monnier et al. 2007). In rapidly rusting iron it is an oxidiser in the wetting phase of wetting/drying corrosion cycles, when oxygen is less readily available as it has to access the surface through pores in the rust layer (Hoerlé et al. 2004) (see 2.1). The reduced form of γFeOOH is an electronic conductor. It is unstable with respect to αFeOOH but remains in rust layers for some time.

2.4.5 Fe_3O_4 (Magnetite)

This black mixed oxidation state compound (Fe_2O_3.FeO) occurs when there is a limited supply of oxygen in the reaction environment (Fig. 2.10). Its occurrence under coatings can be expected where oxygen ingress is limited. Fe_3O_4 often occurs in tandem with αFeOOH, as slight variation in the supply of oxygen will lead to the stability of one or other of these compounds (Fig. 2.10). It can occur in a powdery voluminous form or as a dense layer, which is more common on buried archaeological material (Neff et al. 2007). It is a conducting oxide that ‘almost displays metallic properties’ (Cornell and Schwertmann 2003, 115), which allows it to act as a surface for cathode reactions remote from anode sites (Jones 1992, 405). It can also adsorb chloride onto its surface and may act as a source of mobile chloride in aqueous systems (Ardizzone et al. 1983). It can reduce oxygen more than the metal and residues of it beneath paint layers may lead to corrosion continuing under the film, since it can act as a remote cathode to inward diffusing oxygen (Cornell and Schwertmann 2003, 500).

2.4.6 α-Fe_2O_3 (Haematite)

Haematite occurs in high temperature corrosion and may be a likely transformation product when iron oxides are heated at high temperatures (Cornell and Schwertmann 2003). Dehydroxylation of αFeOOH to α-Fe_2O_3 can commence at 85°C (Cornell and Giovanoli 1990) and can occur as a solid state thermal transformation at around 270°C (Cudennec and Lecerf 2005). It is not expected to occur during atmospheric corrosion but flame cleaning of surfaces carried out prior to application of coatings may offer opportunities for its formation, although this will depend on duration of heating and temperature. It is a semiconductor (Cornell and Schwertmann 2003, 115) and is also stable in acid down to pH 4 (Cornell and Schwertmann 2003, 117).

2.4.7 yFe₂O₃ (Maghemite)

This is not commonly recorded as a corrosion product occurring during the atmospheric corrosion of iron as magnetite is the more commonly identified product. It has been detected on atmospherically corroded historical iron in its more lightly corroded areas (Maréchal et al. 2007) and several times on archaeological objects (Neff et al. 2007). yFeOOH may occur in wet dry cycles (Lyon 2010; Hoerlé et al. 2004) as it is a preferred route for Fe_3O_4 and may be produced in the drying phase as reoxidation of Fe_3O_4. It is relatively resistant to reduction and becomes a more stable part of the rust layer (Lyon 2010).

2.4.8 Ferrous and ferric chlorides

Ferrous chloride solutions can exist in moisture layers on iron highly contaminated with chloride and solid $FeCl_2.4H_2O$ has been detected in pits during post excavation corrosion on archaeological iron, which normally has a high chloride content derived from ingress of Cl^- as a counter ion in burial contexts (Thickett 2011). It forms acidic solutions and hydrolyses to produce low pH values. It is hygroscopic and as $FeCl_2.4H_2O$ promotes corrosion of iron down to 20% RH (Watkinson and Lewis 2005b; Turgoose 1982b), with corrosion ceasing below this RH as $FeCl_2.2H_2O$ becomes the stable phase (Watkinson and Lewis 2005b). So called ‘weeping’ on archaeological iron involves aqueous blisters of ferrous chloride/ferric chloride solution that form a skin of βFeOOH on their surface where abundant oxygen oxidises the solution forming hollow shells when the water within them evaporates (Selwyn and Argrylopoulous 2005). Ferrous chloride solutions can oxidise to form βFeOOH in the atmosphere at high humidity, which will bind up some chloride in its tunnel structure but will present corrosion risks to iron (see 2.3.3). Overall, these soluble chlorides are dangerous corrosion products and can disrupt coatings appreciably.

2.5 Corrosion context

The outcomes of differing corrosion routes and the challenges presented by heritage objects are evident when examining the brine tank from the Lion Salt works Cheshire (Fig. 2.11). For historical, ethical and visual aesthetic reasons preservation of the remaining paint may be a desirable conservation option, while applying a new protective coating to the areas where the metal is exposed. This presents challenges for surface preparation to receive the coating and development of strategies to deal with the existing paint layers, where an industrial approach would be to strip to bare metal or even replace the metal panels where corrosion is extreme.

A range of corrosion has occurred on the tank. Design features such as overlapping plates and riveted joints in conjunction with damaged coatings can lead to oxygen starvation cells being set up (Fig. 2.12) (see section 2.1). In this instance, coating damage at an overlap allows moisture to enter between plates of wrought iron and general corrosion ensures. This depletes oxygen and creates an anode by oxygen starvation. Oxygen replenishment to the interface region is via the overlap creating a highly oxygenated electrolyte at the edge of the overlap and this supports the cathode reaction. This will be activated by wet dry cycles and lamellar corrosion results at the edge of the overlap, due to transport of the Fe^{2+} ions from the anode to the cathode where they react with cathodically generated OH^- ions (Fig. 2.12). Where the protective coating fails, capillarity will draw water into the gap between the plates and corrosion products hydrate thereby maintaining the electrolyte solution. The disruption this produces is evident in Figure 2.11 and 2.13, where whole lines of rivets and plate overlaps show loss of paint and corrosion. Rain events influence oxygen starvation cells such as the one described here, as once the gap between the plates dries corrosion will cease. For the brine tank, object function may also influence corrosion. It contained brine and loss of paint at the overlap may have resulted from seepage of the brine from the inside of the tank providing an electrolyte in the overlap (Fig. 2.13).

Figure 2.11 *Wrought iron brine tank at Lion Salt works Cheshire.*

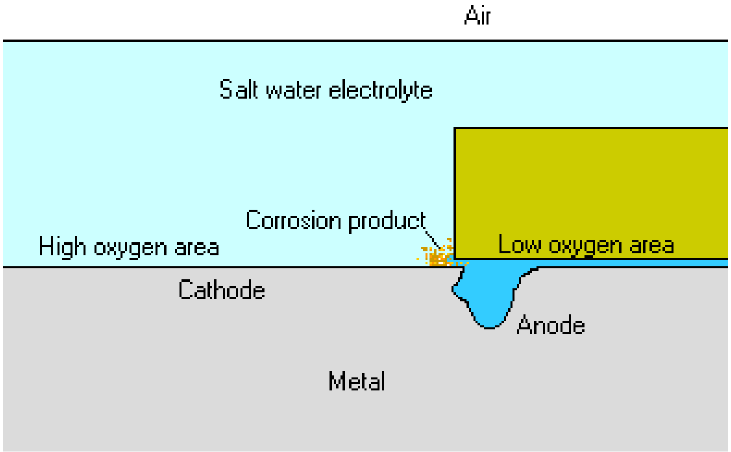


Figure 2.12 *Oxygen starvation cell.*

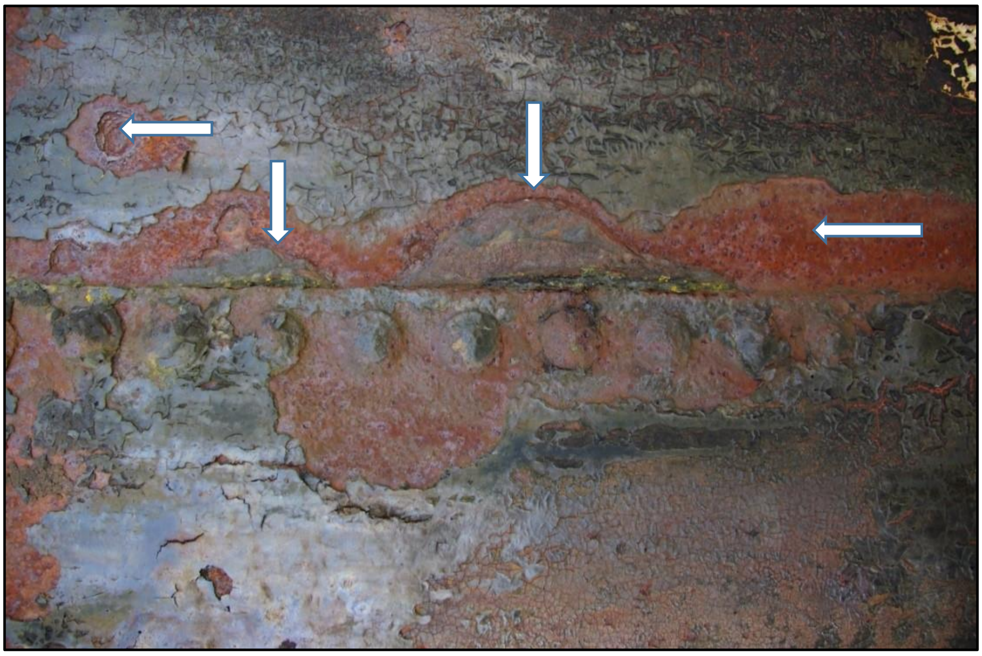


Figure 2.13 *(i) Lamellar corrosion* ⇩ *(ii) pitting corrosion* ⇦

Lamellar corrosion is a common feature of wrought iron corrosion. When coatings are in place it develops by oxygen disbondment beneath the paint layer (see section 2.1). Brunel's 1843 wrought iron ship ss Great Britain was stored for many years open to the elements in a dry dock in Bristol. Attempts to protect it from corrosion using flame cleaning and coatings (Keystone 1999) were ineffective and flaking of the paint layers revealed lamellar corrosion. This layer contained magnetite due to the low oxygen levels beneath it during the corrosion process (Fig. 2.14). Corrosion would have been exacerbated by chloride from the marine environment the ship operated within being present beneath the paint layer, where it offered an excellent electrolyte (Watkinson and Lewis 2004). The impact of extensive wetting and drying cycles from rain events in the uncovered dry dock provided the aqueous phase necessary for corrosion via water running down the hull and as driving rain. Corrosion is now controlled by desiccation within a protective envelope which meets aesthetic, ethical and financial goals by providing excellent visitor access (Watkinson and Tanner 2008).

Solving the problem of hull corrosion above the waterline was directed more towards commercial practices with cleaning to Sa2.5 and two pack epoxy resin with a polyurethane (PU) overcoat. This may be considered less ethical and more intrusive an approach but cost-benefit calculations and pragmatic decisions on maximising the lifespan of the hull and its maintenance regime are of equal importance within conservation strategies. Rationalising such decisions can only occur with confidence in the degree of predictability and for this to occur an evidence base is required. This dissertation sets out to contribute to developing such an evidence base for use of coatings on heritage wrought iron.

Figure 2.14 *Brunel's ss Great Britain paint loss and lamellar corrosion.*

Selection of coatings for ferrous metals is complicated by the range of conditions to which the ironwork will be exposed (Table 2.2). Clear differences could be expected between inland and marine contexts but even on the same site corrosivity conditions may change dramatically, for example with the introduction of de-icing salts on roads in winter. Effective decision-making in selecting a fit-for-purpose coating system must therefore be based on nuanced understanding of corrosion parameters and the specifics of the material and site.

Corrosivity category	**Loss of low-carbon steel after first year of exposure**		**Typical exterior environments in temperate climates**
	Mass loss (g/m^2)	*Thickness loss (μm)*	
C1 very low	≤ 10	≤ 1.3	-
C2 low	> 10 to 200	> 1.3 to 25	Atmospheres with low levels of pollution. Mostly rural areas.
C3 medium	> 200 to 400	> 25 to 50	Urban and industrial atmospheres, moderate sulfur dioxide pollution. Coastal areas with low salinity.
C4 high	> 400 to 650	> 80 to 200	Industrial and coastal areas with moderate salinity.
C5-1 very high (industrial)	> 650 to 1500	> 80 to 200	Industrial areas with high humidity and aggressive atmosphere.
C5-M very high (marine)	> 650 to 1500	> 80 to 200	Coastal and offshore areas with high humidity.

Table 2.2 *Corrosivity categories of exterior environments according to BS EN ISO 12944-2:1998 (British Standards Institute 1998).*

Coating performance and corrosion of iron are interlinked and involve multiple variables that make predicting service life difficult and unreliable. The impact of this on management and best use of available budgets is significant and delivering a message of limited-predictability to the heritage sector managers, when they want quantitative answers, is a major challenge when developing standards for heritage contexts. Predicting coating performance on ‘polished factory perfect un-corroded’ iron surfaces has potential for error, given the range of variables involved, for heritage coatings covered in oxide this unpredictability escalates. For these reasons, this dissertation focuses initial surface preparation methods on genuine heritage iron samples before addressing coating performance.

3 Corrosion Prevention Treatments

3.1 Traditional treatment of wrought iron

Recognition that corrosion of iron degrades its useful properties leading to failures of structures and objects is long standing with treatments applied to wrought iron historically to prolong its useful lifespan. Surface preparation would involve scraping, pickling and chipping to remove scale and contaminants then application of linseed oil, heating of the iron and thorough working of a beeswax and boiled linseed oil mixture into the metal surface (Kreislova et al. 2013, 333; Ashurst and Ashurst 1988).

As now, corrosion prevention commonly involved application of protective coating systems. Traditionally, topcoats were of oil based paints with turpentine solvent, linseed oil binder, white lead pigment (carbonates and sulphates) plus additional pigments and driers (Blackney 2010). Corrosion inhibiting primers in the 17th and 18th centuries contained red ochre, white lead and occasionally the red lead that would become the first choice of anticorrosive pigment in the late 18th and early 19th centuries (Kreislova et al. 2013, 333; Blackney 2010). Red lead has a strong affinity for linseed oil and a tendency to form lead soaps in a tough, elastic and impermeable film (Gayle et al. 1992, 137). Pitch, coal tars and bitumen were alternative coatings for larger structures such as bridges, piers and aqueducts (Blackney 2010). Waxes and oils may have been used on bare metal and working machinery parts. Bitumen was identified as the protective coating on a brine tank from a salt works in Cheshire (Fig. 3.1).

Figure 3.1 *Bituminous coating on a brine tank in Cheshire.*

A rich resource for examining historic coating practices exists on wrought iron structures. Where surface preparation before recoating has been minimal, a chronology of paint layers remains beneath more recently applied coatings. Even prepared surfaces retain vestiges of historic coatings in inaccessible areas. When examined in cross section, these coating layers allow analysis of compositional and aesthetic changes over time. Taking colour as an example, a relatively recent preponderance of black coatings on wrought iron belies earlier trends towards greater colour diversity. Combining study of historic sources and paint layer sections allows identification of early 18th century regional trends for blue, green, grey or stone colours and a dominance of green by the end of the century (Catt 1995, 19). When selecting colours for wrought iron coatings, inspection of paint sections permits restoration of an original or historic aesthetic. Traditional green railings can be seen at the English Heritage property Apsley House in London. Figure 3.2 shows multiple paint layers resulting from many overcoating episodes on the Tijou screens at Hampton Court Palace and on railings at Dunbar Castle. Between 20 and 30 coatings can be identified on the Tijou paint section and 16 on the Dunbar section. Striking colour variation is evident in the Tijou section until the uppermost layers of black coatings. The bright yellow and red layers near the top of the section are likely primers. The potential of such sections to inform on practicalities and failure of coatings is explored in 3.3.

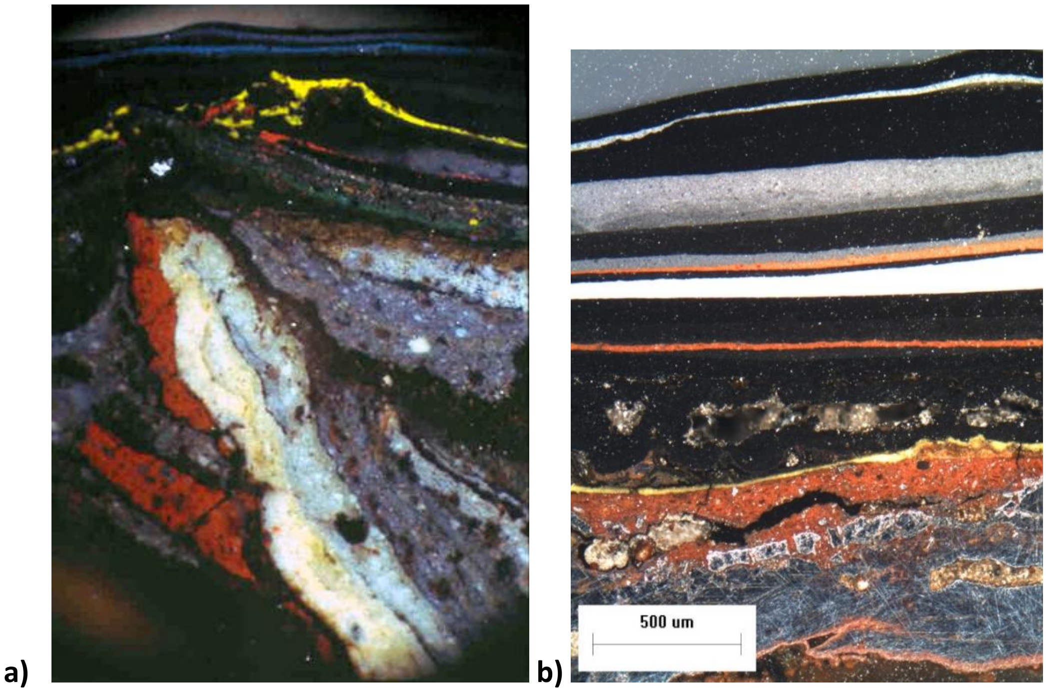


Figure 3.2 *Polished section of paint layers from:* ***a)*** *the Tijou screen at Hampton Court Palace (http://patrickbaty.co.uk/2010/11/25/hampton-court-palace-2);* ***b)*** *railings at Dumbarton Castle (courtesy of Amber Lawson).*

3.2 Current practice

Modern techniques for corrosion prevention of historic wrought iron continue to centre on application of protective coatings following a degree of surface preparation. Obtaining a clean substrate surface is thought critical for successful corrosion prevention by coatings (Ross 1977, 29; Trethewey and Chamberlain 1995, 320; Leighs 2008a) but what constitutes adequate and appropriate preparation for historic material is a grey area. Industry based standards are the main guide but their translation to heritage contexts and materials is not simple (3.4.3). Heritage ironwork practitioners, having arguably the greatest experience of treating historic wrought iron, have outlined common practice in online guidance (Blackney 2010; Meehan

2010; Taylor and Suff 2010; Topp 2010) and in personal communications. Methods are reported here. Where discussion is supplemented by other references, these are given.

3.2.1 Recording and dismantling

Where possible and necessary, structures are recorded and dismantled for treatment off site. This facilitates full condition assessment and thorough cleaning. Recording includes drawing with measurements, photographs and details of repair methods employed. Mechanical joints which are simple to remove may be difficult to reinstate hence no more dismantling than strictly necessary is recommended.

3.2.2 Cleaning and surface preparation

There is much debate over necessary preparation levels for surface tolerant paints (Higgins et al. 2010, 2484). Reports insist even minor contamination by oil or grease prevents successful adhesion and hygroscopic pollutants (chlorides and sulphates) draw moisture through holidays and pores in coatings (Godfraind et al. 2012, 180). For non-surface tolerant coatings a surface free of oxides, contaminants and grease is demanded by manufacturers for successful coating performance (Leighs 2008a). Removal of existing surface coatings and corrosion products is therefore common practice prior to repair and recoating with all coating types. This also facilitates repairs, removes hazardous residues of lead based paints and reveals detail obscured by coatings.

Difficulties arise where historic paint layers are viewed as valuable evidence and original material. Ethical conservation practice may not permit removal of such coatings. A trade-off exists between increased efficacy of coatings applied to thoroughly prepared surfaces and the ethics of removing historic material as coatings and surface oxides which may also be protective. A range of minimally-destructive cleaning techniques (Table 3.1) may prepare surfaces adequately for successful application of surface tolerant coatings by removal of (Childs 1985, 26):

1) Mud and disfiguring deposits which trap moisture;
2) Soluble salts which encourage electrolytic corrosion;
3) Grease/oils which stain coatings and inhibit adhesion.

Material	**Removes**	**Advantages**	**Do not use on**
Emulsifiable solvent systems (white spirit & emulsifier)	Thick oil, grease and dirt	Can be used on metals and most paints	Associated organic materials – textiles, rubber
Aqueous alkaline/ detergent (sodium hydroxide type)	Oil grease and dirt	Effective on bare ferrous metals	Aluminium or tinplate elements, galvanised iron, organics
Sugar soap	Light coatings of oil, grease, dirt	Inexpensive and easy to use	Some paint films become softened
Detergents	Light coatings of oil, grease, dirt	Effective on most surfaces	Some paint films or where frothing is a problem
Organic solvents (paraffin, white spirit)	Oil, grease but not dirt efficiently	Good degreasing action but may smear oil over wider area	Organic materials or areas difficult to rinse

Table 3.1 *Summary of some non-destructive surface cleaning methods, their applications, advantages and disadvantages after Childs (1985, 26).*

Where more destructive surface preparation is permissible/desirable, methods include hand and power tools (scrapers, wire brushes, needle guns), chemical stripping, flame cleaning, air abrasion (shot and grit blasting) and high pressure water blasting. Grit blasting to Sa 2.5 or 'near white metal' (British Standards Institute 1998) is common for removal of existing coatings and oxides but damages iron surfaces and removes manufacturing and working evidence. Consequently, chemical removal of paint may be advocated. Paint type dictates the chemical used which must be thoroughly rinsed after cleaning and constant widening of health and safety regulations reduces options for removal. Heritage ironwork practitioners recommend removal of corrosion products by application of heat (flame cleaning).

This exploits the differential in expansion of iron and iron oxides to remove corrosion products from iron surfaces.

Practical considerations in selecting surface preparation methods include health and safety concerns, cost, equipment, expertise and preparation for waste management (spent blast media and coatings, residual chemicals from stripping baths, debris containing toxic heavy metals such as lead from coatings). Appendix 1 summarises guidance on surface preparation methods from heritage sector texts (Wilson et al. 2008; Childs 1985; Ashurst and Ashurst 1988; Godfraind et al. 2012). Although there is broad agreement between authors, suitability of blasting with 'hard' media is recommended by one author and not by two others. There are slightly divergent parameters for success according to the priorities of the authors. This encourages treatment specifiers to consider a range of factors but confuses decision-making processes. Guidance is neither clear nor standardised.

3.2.3 Repairs

Repair using the same material and techniques as employed for original manufacture of the object or structure are deemed desirable. Dominant considerations when selecting repair and replacement material are durability, price, corrosion resistance, strength, ease of working, compatibility with adjacent materials and availability. In reality, price of a job likely plays the biggest role in decision-making, particularly since councils and government departments are often the specifiers. Tendering for contracts demands competitive pricing which narrows the options for materials and processes.

The availability of wrought iron for conservation is due to its recyclability. Early charcoal iron is a limited resource but 19th century material is abundant and can be reforged for repairs. Much derives from dismantled historic bridges and similar structures. The variable quality of historic wrought iron should be considered when selecting material for repairs. Some practitioners advocate use of pure iron which is argued to permit higher quality welds and conforms to ethical requirements that repair material be distinguishable from original. Mild steel is often used but it performs differently to wrought iron, does not lend itself to the same forging techniques (necessitating arc welding) and rolled sections are uniform and easily recognisable from hand forged wrought iron. This may not be at odds with conservation ethics but delivers an undesirable aesthetic. Malleability permits deformations in original material to be straightened which avoids replacing sections.

Bolts, rivets, collars and traditional fire or forge welding are recommended and resetting of iron fittings in stone using molten lead in preference to historically inaccurate resins. Areas acting as water traps may be modified to enhance drainage, flooded with paint or packed with red lead putty or pitch. Modern fillers (acetic acid free RTV silicone rubbers, polysulphide mastics and epoxy or polyester resins) are compatible with most modern protective coatings.

3.2.4 Protective coatings

Application of surface coatings to minimise corrosion is advocated and the range in use is briefly summarised here. Traditional oil based systems (or modern alkyd equivalents) are recommended with two-pack epoxy systems with polyurethane topcoats to be used on exposed sites or where maximum longevity is required (up to 25 years). Lead based paints can be licensed for use on Grade I and II* listed buildings in England and Wales and category A in Scotland (Historic England 2015). Traditional oil paints had become unpopular due to labour intensive application of many thin, slow drying coats. A trend towards traditional and sympathetic materials and historic paint schemes renewed their popularity. They offer advantages of compatibility with existing coatings and tolerance of surface oxides. Coatings with alkyd oil binders largely replace traditional oil paints having advantages of higher film thicknesses (permitting application of fewer coats) and faster drying times. They do not offer as long a service life as epoxy resin coatings but maintenance is simple and coatings widely available. Other single pack coatings with increased service life are solvent drying vinyls, chlorinated rubbers and moisture-curing polyurethanes. Waxes and oils conform to minimum intervention and reversibility conservation ethics but are not recommended for exterior wrought iron.

Galvanising is considered inappropriate for historic wrought iron as the necessary acid dipping etches the surface, can damage delicate elements and is difficult to rinse thoroughly. Galvanising is clearly very difficult to reverse. Zinc or aluminium sprayed coatings are occasionally applied to cathodically protect grit blasted wrought iron but spraying in situ presents difficulties.

3.2.5 Application of protective coatings

Methods should follow those stipulated on manufacturer data sheets with strict adherence to conditions of temperature and humidity. Roller and spray application are faster but brush application likely results in more attention to joints, crevices and inaccessible areas. Film thicknesses should be carefully controlled to conform to manufacturer instructions and breaks or pinholes in the coating (holidays) be avoided.

3.2.6 Maintenance

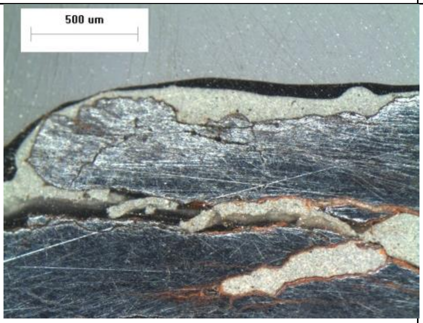
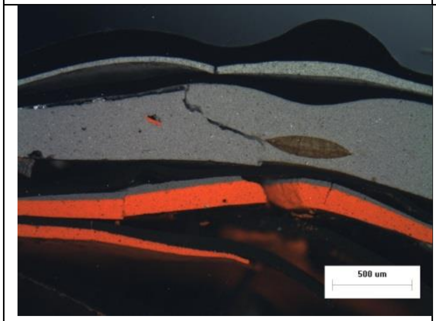
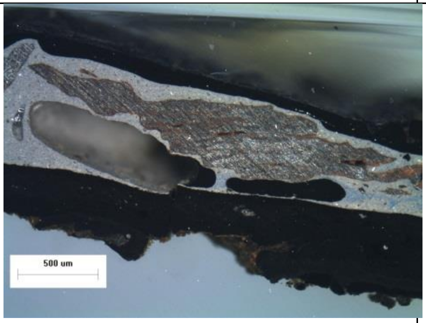
Conservation of exterior wrought ironwork must be an ongoing process not a discrete event and this should be identified in management plans. Systematic maintenance regimes are required involving periodic inspections, written repair schedules, dedicated and adequate budgets and trained staff. Inadequate maintenance, often due to lack of time, funding and long term vision, eventually necessitates costly and highly interventive conservation and restoration projects which could be avoided. Alternatively, the iron is lost from the heritage pool. A suggested maintenance schedule is given in Table 3.2.

Twice yearly (spring/autumn)	*Biannually*	*Occasionally*
General inspection Record areas of concern Touch up damaged coating Clear gutters and rainwater goods Remove debris Check drains and soakaways Secure loose components Clean and lubricate working parts Remove snow/ice/de-icing salts	Minor repairs Inspect seals and renew as necessary Check iron fittings in masonry for corrosion Repair and renew coatings as necessary	Renewal of coatings – timescales dependent on coating, atmospheric corrosivity, use of the structure, extent and quality of surface preparation

Table 3.2 *Suggested schedule of maintenance of exterior wrought ironwork (after Godfraind et al. 2012, 80).*

3.3 Evidence from paint layers in section

Examining paint layers from historic ironwork offers insight into application methods, coating performance and modes of failure. Table 3.3 gives examples of polished sections of coatings from wrought and cast iron and mild steel gates and railings at Historic Scotland properties. Samples were gathered for a parallel project by Amber Lawson examining coating performance on steel substrates but are relevant for this study.

Coating cross section	Comments
	*a) Dunstaffnage Castle chapel gate* Primer application on top of previous topcoat.
	*b) Dumbarton Castle stair handrail* Primer ingress into laminations of substrate. Break-up of the primer where crevice expanding?
	*c) Dumbarton Castle railing* Air bubble evident in thick grey coating from which a crack in the coating has propagated which eventually follows the line of the grey/black coating interface and causes deadhesion. Lack of adhesion evident between most grey and black coating layers and black and red layers.
	*d) Dunglass Church gate* Large air bubble likely formed during coating application. Air bubbles present in a surprising number of sections and are likely not particularly visible during application.

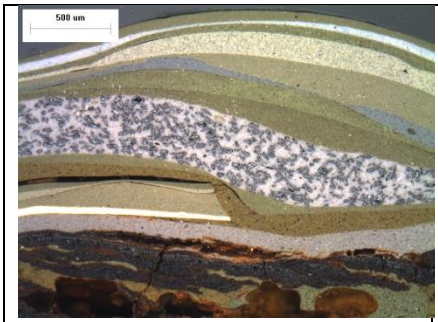
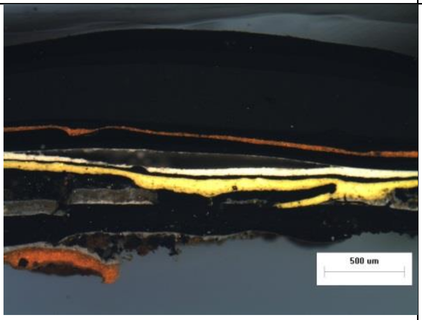
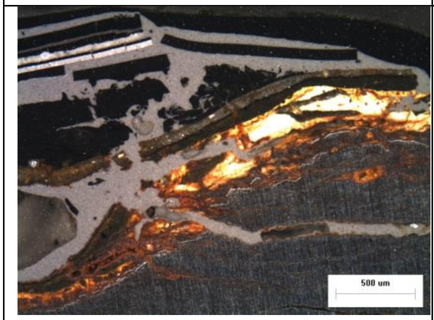
	e) *Fort George railing* Primer application over topcoat. Coating failure/damage with the loss of several layers which are then overcoated. Variation in thickness of layers evident.
	f) *Broughty Castle railings* Cracking and lifting of coatings infilled by next coating application. Demonstrates importance of regular maintenance, touching up to prevent further delamination of cracked coatings.
	g) *Arbroath Abbey railings* Break up of black coating layer indicates embrittlement? Caused by environmental factors or movement of underlying substrate?
	h) *Palace of Holyroodhouse railing water leaf* Delamination between the black and white coating layers. Alternating dark and light colours of coatings permits identification of holidays and missed areas during application.
	i) *St Andrews Cathedral gate* Consolidation of fragmentary coating layers by subsequent coating application. Corrosion products also consolidated and coating ingress into crevices in substrate is evident where air bubbles have formed.

Table 3.3 *Microscopy images of polished sections of coatings from wrought and cast iron and mild steel railings and gates from Historic Scotland properties (courtesy of Amber Lawson) highlighting aspects of application, performance and failure. Scale bars are 500µm.*

Discussion of samples a)-i) offers insight into the range or absence of surface preparation and the evidently ad hoc approach to recoating. Polymeric coatings are applied to a dynamic substrate. Expansion and contraction of the iron with temperature fluctuations tests the physical properties of coatings. Sections f), g) and i) show cracking of coating layers possibly resulting from substrate movement coupled with polymer weathering and embrittlement. Break-up of the black layers in i) may be caused by corrosion product growth and associated volume changes below the coating. In section b) widening of the crevice in the substrate has fractured and de-adhered primer from within the crevice leaving cracks permitting ingress of water.

Surface preparation of i) prior to application of the grey coating (likely primer) was limited as evidenced by fragmentary coatings and corrosion products below it. The newly applied primer layer might seem to be sitting above these as a layer yet the primer was sufficiently low viscosity to be drawn into crevices and make contact with the metal substrate. It also has a consolidating effect on the fragmentary layers.

Air bubbles in coatings are evident in sections c), d), e), i). These are sites of weakness with cracking propagating from a large bubble in c) eventually causing de-adhesion between layers. Air bubbles are likely invisible to practitioners applying coatings but potentially undermine protection. Two pack coatings may be more susceptible to air bubbles given extensive stirring to mix two parts. Single packs are stirred to a lesser extent before application to counter settlement of solids and separation of coatings. This may also cause bubbles. Application of more, thinner layers may mitigate the problem of large bubbles.

Sections a), c), e), f), h) and i) show minimum surface preparation leading to application of primer over pre-existing coating systems. If these primers protect substrates by sacrificial or inhibitive mechanisms, contact with the substrate is essential for performance. They cannot be expected to protect effectively when applied over existing coatings.

Use of contrasting colours for consecutive layers in a system is evident in these sections. This is advantageous for assessing successful overcoating and is clearly common practice whether through deliberate selection or manufacturer design.

Sections offer insight into practicalities and performance of coatings and application methods which cannot be seen in plan view. These are not generally available to practitioners to inspect their own work but could be a useful tool for generation of illustrated best-practice guidelines for coating of historic wrought iron. A striking observation from these cross sections is the range of coatings and apparent cavalier attitude to recoating. This lack of surface preparation means that the rheology of the coating system and the ambient environment (RH, temperature, precipitation) will be important for any successful outcome. There will also be no degree of predictability attached to the coating performances in the long term.

3.4 Decision-making in conservation of historic wrought iron

3.4.1 Decisions and decision-makers

Historic wrought iron is ubiquitous in Western Europe and structures of this material may be set apart from other museum-type object by their scale, complexity and exposure to uncontrolled, exterior atmospheric conditions. Costs associated with treatment and maintenance can be prohibitive and procedures are frequently more interventive and ad hoc than conservation ethics advocate. Mechanisms of corrosion and corrosion prevention by protective coatings are complex and not fully understood even within the sector dedicated to its research. Responsibility for planning or specifying its treatment belongs to a range of individuals who may or may not have experience of heritage iron or a working knowledge of conservation principles. This includes home owners, museum professionals, house managers and property surveyors. Realpolitik often dictates that there is no budget for specialist consultation prior to specifying conservation work for historic wrought iron, yet it involves a large number of variables including choice of surface preparation methods, coating systems and maintenance regimes whose interrelations complicate decision-making (Figs 3.3-3.5).

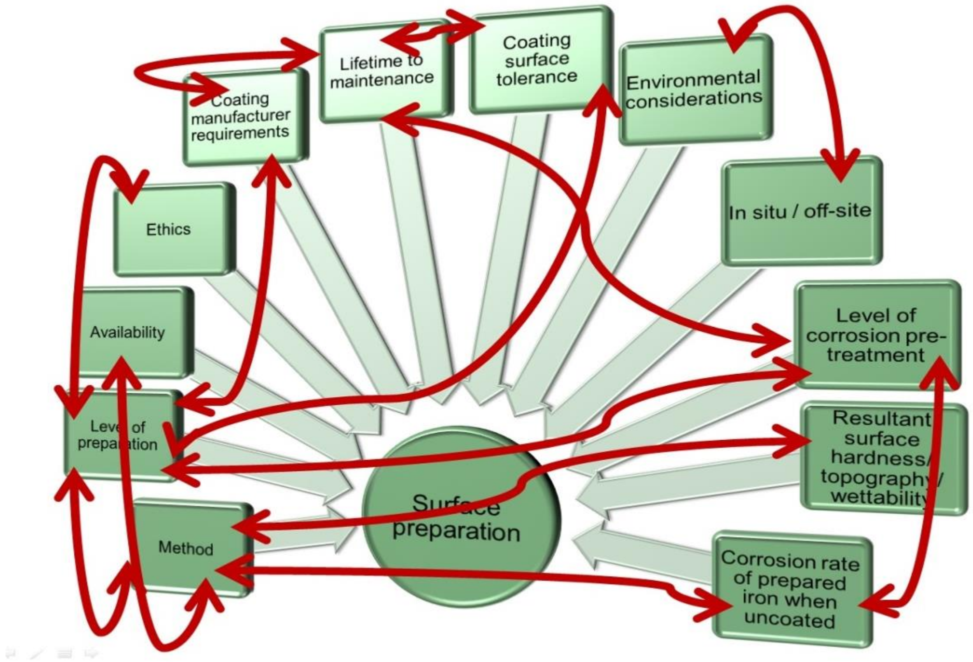


__Figure 3.3__ Interrelating factors (red arrows) in selection of surface preparation method.

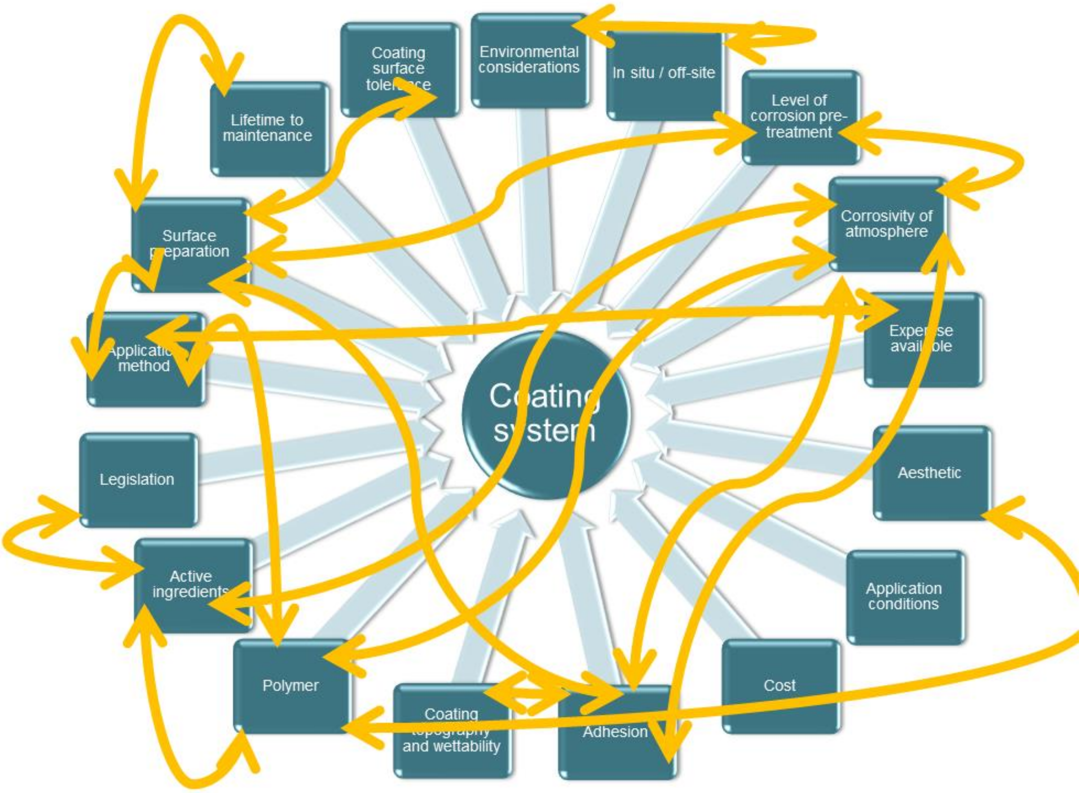


__Figure 3.4__ Interrelating factors (yellow arrows) in coating system selection.

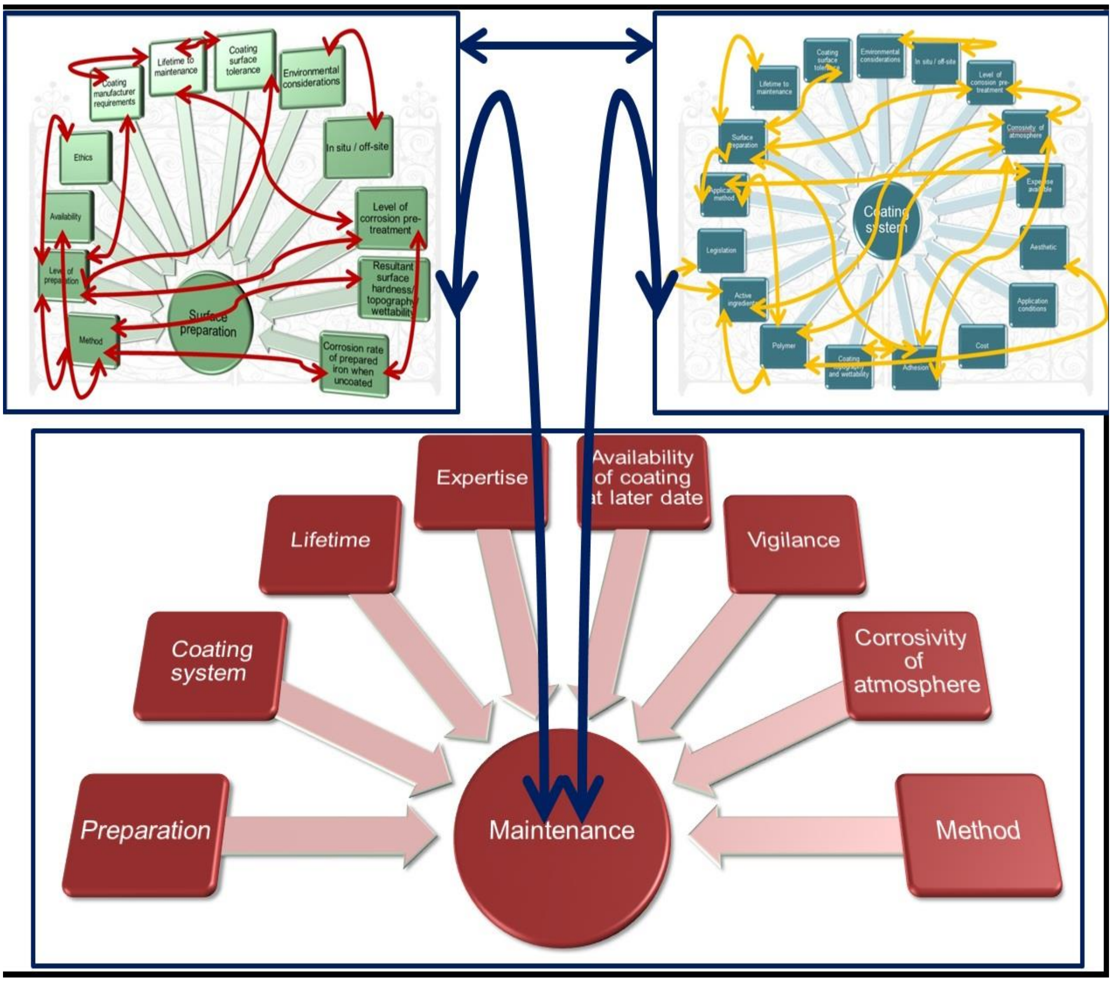


Figure 3.5 *Diagram indicating the complexity of the decision making process for treatment of historic wrought involving many interrelated factors. Arrows indicate a relationship between factors.*

Due to heavy reliance on tendering in this part of the heritage sector, specification for treatment of wrought iron often falls to a range of individuals whose familiarity with historic materials and structures and conservation practice and ethics is limited. The most basic step in the decision-making process, identifying wrought iron from mild steel or cast iron, can be difficult for the non-specialist especially when sampling is not feasible and decisions are made on visual appearance, technology and corrosion patterns. Even where treatment is by conservation specialists, sector specific research to aid their choice of paint and treatment system is sparse and quantified data is absent entirely. Negotiating the complex web of treatment variables depicted here and juggling one factor against another for positive outcomes without essential underpinning evidence is extremely challenging.

3.4.2 **Guidance**

Written guidance is available in the form of technical bulletins, leaflets, short articles, book chapters and occasional case studies in specialist journals and conference proceedings (Ashurst and Ashurst 1988; Barker 2010; Blackney and Martin 1998; Blackney 2010; Cheltenham Borough Council (online); Davey 2007; Davey 2009; Meehan 2010; Mitchell 2005; Taylor and Suff 2010; Topp 2010; Schütz and Gehrke 2008; Watkinson et al. 2005; Wilson et al. 2010) published by heritage bodies, government agencies, local councils and heritage ironworkers.

An overall absence of evidence based heritage standards for the treatment of historic wrought iron means decision-making is reliant on un-scaled comparisons and, at worst, guesswork. Although detailed industrial and commercial standards and guidelines exist (ASTM 2008; British Standards Institute 2000, 2005/2006, 2006/2007, 2012; Corus 2004), their focus on modern materials, without any ethical constraints of the type found in conservation, limits their direct use in historic contexts to specific situations.

The heritage sector guidance on surface preparation listed above is well-intentioned but limited in scope, frequently conflicting and reliant on an evidence base that is rarely quantified or offers data and methodologies that are difficult to translate into practical contexts. It is entirely understandable that application of this guidance becomes anecdotal or experience-based on many occasions. Identifying how to generate the necessary quantitative evidence based data that will transform practice will rely on well designed, and preferably co-ordinated, research. Unfortunately, conservation of large heritage wrought iron assemblages is dominated by contractor-based private sector activity; understandably, research is not a priority here and gaining funding to support it is extremely difficult. Similarly, research within commercial coating companies and national standards bodies into developing evidence based, dedicated procedures and products for historic material is hampered by the lack of potential profit in the heritage sector. This leaves the beacon of research to be borne by academia and the heritage institutions themselves, where it must exist amongst many other priorities and be subject to underfunding. A natural outcome of this situation is that surface preparation techniques developed for industrial contexts are employed in the heritage sector, despite a dearth of study into their suitability for historic wrought iron. The upshot is that the surface preparation of heritage iron to receive paint is unregulated, ad hoc and unable to support predictive conservation procedures. Exceptions occur when industrial standards can be adopted and adhered to; the wrought iron hull of Brunel's ss Great Britain was cleaned to Swedish Standard Sa 2.5 (ASTM 2008) prior to painting, as befitted the ethical constructs in place for a corroded hull that had been cleaned to the metal and painted periodically during its lifetime (Watkinson et al. 2005).

3.4.3 Use of standards in heritage contexts

Conservation decisions are necessarily being made on the strength of anecdotal reports of successes and failures. This limited understanding of the effects of treatments applied to heritage material is in direct contravention of sector codes of ethics as set out in national standards, which advocate evidence based treatment techniques delivered within ethical constructs (Canadian Association for the Conservation of Cultural Property 2000; American Institute for Conservation of Historic and Artistic Works 1994; International Council of Museums 1984). For instance, the availability of empirical evidence relating selection of surface treatment methods and protective coatings to the corrosion rates of historic wrought iron is non-existent, yet this information is the key to delivering evidence based management of our ferrous metal heritage. If the limited resources available for heritage preservation across the globe are to be employed to best effect, informed and predictive management strategies are essential.

This approach requires heritage specific guidance that can be utilised internationally across the sector, much as industry uses agreed international standards to dictate procedure for surface preparation, coating application and coating performance. The stringent stipulations of coating manufacturers and the existence of international industrial standards guide practice in the protection of modern steels, producing a heavily regulated industry where best practice methodologies for surface preparation and application of protective coatings are clear for practitioners (Standardiseringskommissionen i Sverige, et al. 1980; British Standards Institute 2007). Coating manufacturer datasheets recommend suitable coatings for steel substrates in various corrosive environments and specify appropriate surface preparation and application methods according to these standards. The emphasis here is on strict preparation protocols to support the claimed longevity of coatings.

In contrast to industry, heritage preservation is a poor relation with neither regulation nor its own industry focused standards. Despite offering a rich source of information, caveats prevent wholesale application of the international corrosion prevention standards and guidelines to heritage contexts. First, these international standards for surface preparation are scaled by the corrosion performance of mild steel. While this may be applicable to many heritage contexts dating from the twentieth century, mild steel having replaced wrought iron in many construction applications, each material exhibits different composition, microstructure and corrosion mechanisms (L'Héritier et al. 2013; L'Héritier and Dillmann 2005; Gandy 2007; Santarini 2007). Second, industry as relates to modern construction is not hampered by the ethical and aesthetic constraints applicable to heritage ironwork practitioners which are set out in national standards. For example, coating manufacturers regularly specify blasting to Sa2.5 or 'near white metal' to produce a surface profile promoting coating-substrate adhesion. For the heritage industry, loss of original material associated with blasting to a metal core (where this exists) conflicts with concepts of 'limitos' and preservation of original surface (Bertholon 2001a, 2001b, 2007). The perceived advantages of achieving the most suitable surface for optimal performance of new protective coatings to ultimately minimise loss of metal mass through further corrosion, must be weighed against decimation of information held within historic coating and corrosion product layers. Little quantitative information exists regarding the impact of aggressive surface preparation techniques on heritage metals.

A recent extensive survey of references to the use of national and international standards cited in metal conservation literature, covering the period 1995-2010, revealed only two instances of citations of surface preparation standards for heritage ferrous metals (Argyropoulos et al. 2013). Why is there a lack of engagement with existing industrial standards in heritage conservation; is it an indication of a lack of standardisation in metal conservation practice, an indictment of standards which are not fit for purpose within heritage contexts or simply that there is limited reportage of current practices? Whatever the reason, the applicability and usefulness of the standards employed in the corrosion protection sector to heritage contexts need to be explored, if they are to be recommended as meeting the particular needs of ferrous metals in heritage contexts. Research delivering quantitative data is required to fulfil these goals.

A first step towards achieving this is to use international standards to determine how surface preparation methods used in these contexts influence corrosion rates of the ferrous metal substrate. This is fundamental to evaluating the likely efficacy of a coating system, as transmission of reactants through coatings will result in corrosion related to the reactivity of the underlying surface. Corrosion will impact on the deterioration and loss of the overlying coating subject to the input of other variables such as its adhesion to the prepared surface. Clearly, a wide range of interrelating factors determine coating performance but surface preparation remains a fundamental variable within the equation.

Selection of protective coatings from a saturated market of heavily promoted products is equally unstandardised. Fashions within the protective coating sector and heritage practitioner circles influence choices but empirical evidence of performance on historic materials is utterly absent. Two-pack epoxy resins found favour in heritage after well-publicised projects promoted their credentials. Today, questions are raised over their suitability for application to intricate and dynamic heritage ironwork subject to contraction and expansion in different planes, their ‘plastic’ appearance which jars with the historic aesthetic and high build which disguises fine detail. Low build oil-based coatings had fallen out of favour thanks to their painstaking application in many thin coats. A resurgence of interest in these coatings has arisen out of concerns for compatibility with historic aesthetic and traditional methods.

What cannot currently be introduced to balance these arguments is empirical evidence of corrosion rates, predictions of lifetimes and modes of failure of coating systems when applied to historic wrought iron exposed to atmospheric corrosion. These are all factors to aim for and experimental research should be focused on answering them.

4 Experimental

4.1 Ethos and rationale

4.1.1 Research ethos

Decision-making in treatment of historic wrought iron subject to atmospheric corrosion processes is complicated and evidence of treatment successes and failures to underpin decisions is entirely anecdotal (3.4). Empirical evidence of treatment effects is required to facilitate management decisions and produce cost benefit analysis of options. This approach is applicable throughout the heritage sector which is a cross-over discipline that must be both derivative and innovative. Heritage draws heavily on other sectors but must adapt methods and approaches to historic materials and contexts. The data on which these are based must be both empirical and fit for purpose. Recognition that treatments will in many cases not be specified by conservators or specialist heritage practitioners highlights the need for evidence based guidance that is widely disseminated and accessible both physically and intellectually. It must be balanced to consider divergent priorities of stakeholders and offer a range of considered options that can be tailored to meet constraints of budget, time, resource and available expertise.

This experimental research was designed to produce empirical data of surface preparation and coating selection effects on corrosion rates of historic wrought iron which will underpin published guidelines on best practice. The research was funded by Historic Scotland and builds on earlier work by their Technical Conservation team. It is contextualised by qualitative reporting of practicalities and relates interplay of surface preparation methods and successful application of protective coatings.

4.1.2 Related work

An abundance of historic ironwork exists in Scotland from a tradition of wrought and cast iron production (David Mitchell *pers. comm.*). Acknowledging the variable state of preservation of this ironwork and the predominantly anecdotal guidance for its treatment, Historic Scotland instigated a research programme to assess systematically optimum treatments for cleaning and repairing these traditional materials (Wilson et al. 2010, 248). Investigation of 25 surface preparation techniques for cast iron (Wilson et al. 2008; Wilson et al. 2010) assessed methods according to success criteria including:

- Removal of existing paint;
- Preservation of oxide layers;
- Influence on physical properties (bend strength, micro hardness);
- Resultant surface profile;
- Value for money;
- Operator skill level required.

As a result (see Appendix 1), manual and power tool cleaning were recommended for indoor cast iron, flame cleaning for in situ exterior ironwork and blasting with 'soft' blast media (plastic, walnut shells or dry ice) for workshop procedures. Chemical cleaning (immersion in NaOH, HCl or H_2SO_4/H_3PO_4) was found to require further investigation. Laser cleaning, rotary abrasive disc (power) and wire brushing (manual and power) techniques were found to be unsuitable for further investigation or sole use for cleaning. Whilst offering data (largely qualitative) on effectiveness of methods, the study was limited to cast iron and did not project to real life exposure contexts by examining corrosion rates of differently prepared surfaces. This PhD research was funded by Historic Scotland to address some of these shortcomings.

The research extends the investigation of surface preparation methods to wrought iron substrates. It builds on the previous findings by examining recommended procedures of flame cleaning and blasting with 'soft' media and further investigating chemical cleaning and blasting with 'hard' media (see 4.1.3.2). Physical effects on substrate surfaces were quantitatively examined followed by measurement of their oxygen consumption rate, as proxy for corrosion rate (4.1.3.1), when sealed in individual reaction vessels at high relative humidity (RH). Investigation of coating effectiveness for wrought iron could not produce empirical data for a broad range of coatings given the enormous diversity in use. A contextual approach was taken to selection of relevant coatings for this study (4.1.3.4).

4.1.3 **Rationale for methods and parameters**

4.1.3.1 *Oxygen consumption as proxy corrosion rate*

Surface preparation and application of protective coatings aims to prolong lifetimes of wrought iron structures by minimising or preventing their corrosion. The ultimate measure of success of the treatment is empirical measurement of corrosion rate.

Quantification of corrosion rate can be achieved by measurement of cathodic consumption or production of reaction components (Turgoose 1985, 14). The predominant cathodic reaction in atmospheric corrosion of iron is the reduction of oxygen (Jones 1992, 7). Despite reduction and reoxidation reactions, corrosion products that occur during wet/dry cycles in the atmosphere correlate closely with metallic dissolution at the anode (Hoerlé et al. 2004). Measurements of oxygen consumption of a metallic sample in a given environment can therefore be used to estimate comparatively the extent and rate of corrosion of the metal. The advantages of this method are its non-destructive nature, its relative sensitivity and the lack of need for specialist knowledge.

Amperometric sensors for monitoring oxygen levels are robust, cheap and widely available but consume oxygen themselves (Matthiesen 2013, 365). An alternative method, described by Matthiesen (2007, 272; 2013, 365-371), is based on luminescence with molecules excited by light at one wavelength emitting energy at another (Fig. 4.1). Oxygen-sensitive molecules have been developed for which the presence of oxygen quenches light emission and oxygen concentration can thus be determined by luminescence decay time or intensity of emitted light. The oxygen sensitive compound within the sensors is a ruthenium complex excited by light at 505nm with emitted light measured at 600nm. This ruthenium complex is attached to a polyester base and formed into sensor spots of 5-10mm diameter.

Advantages of such a system include (Matthiesen 2007, 272; 2013, 371):

- No leakage;
- No self-consumption of oxygen;
- High selectivity of measurement for oxygen;
- Versatile reaction vessel dimensions;

- Relatively low cost;
- Sensor spots function in air and water;
- Remote measurement through transparent vessel walls is possible.

The system is not without any difficulties. Measurements are temperature dependent; temperature must be controlled and recorded throughout. Reaction vessel leakage must be measured and accounted for in interpretation of the results. Consumption of oxygen by other components within reaction vessels (e.g. silica gel, dataloggers) must also be measured and subtracted from sample consumption. There must also be a degree of confidence that the corrosion reaction is the only reaction of the sample material that is likely to consume oxygen.

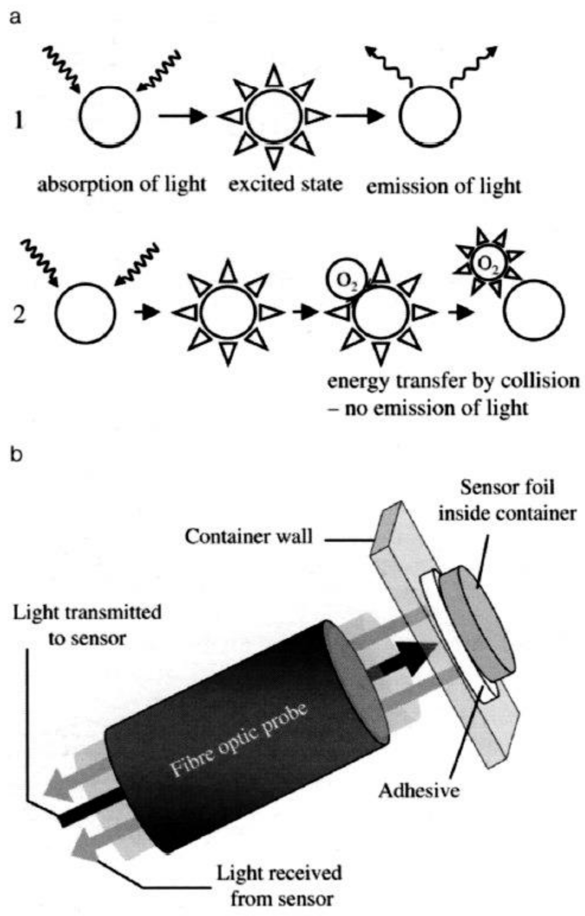


Figure 4.1 a) *working principle behind optical oxygen electrodes. Luminescent compound excited by light at one wavelength is emitted at another wavelength (a.1). In the presence of oxygen the energy of the excited molecule is transferred by collision with oxygen rather than by emission of light (a.2). Oxygen concentration is correlated to intensity of emitted light and luminescence decay time.*

b) *Diagram showing modulated light sent from transmitter to sensor foil via an optical fibre via which the emitted light is also returned. Measurement is possible through a transparent container to sensor spots inside.*

(Modified from www.presens.de and published in (Matthiesen 2007, 272; Matthiesen 2013, 370).

4.1.3.2 *Surface preparation methods*

Flame cleaning and blasting with soft media were recommended in Historic Scotland findings as appropriate for retaining oxide layers. Further testing here examined their suitability for recommendation for wrought iron and investigated corrosion rates after treatment which had not been looked at previously. Crushed walnut shell was selected as the soft media (hardness 3-4 Mohs) having been recommended for cleaning copper alloys (Lins 1992) and having the advantage of biodegradability.

Stipulations by coating manufacturers and in British Standards for surfaces prepared to near white metal (Sa2.5) to optimise coating performance conflict with heritage concepts of oxide layer retention for ethical and corrosion protection reasons. Despite not being recommended by Historic Scotland, blasting with hard media to Sa2.5 in this study examined resultant surface profiles for coating adhesion and corrosion rates relative to substrates with oxide layers retained.

Chemical cleaning was found by Historic Scotland to require further testing. Sodium hydroxide has long been known as a corrosion inhibitor for ferrous metals (Mayne and Menter 1954; Mayne et al. 1950; Turgoose 1985) and with the probability of its solvent effect on existing paint layers, was selected for testing here.

4.1.3.3 *Humidity*

Potentially conflicting priorities exist in laboratory testing of corrosion rates. Aims to produce measureable corrosion of uncontaminated samples in a relatively short duration experiments may be incompatible with an ethos of modelling real-life contexts (Leygraf and Graedel 2000). Fortuitously, climatic conditions in Britain involve relative humidities above 80%RH as an annual average and in winter months in the region of 84-86% (Met Office 2014) (Table 4.1).

Region	**Average Relative Humidities 1981-2010 (%)**		
	Annual	**Oct – Mar**	**Nov – Feb**
East Scotland	81.41	83.53	84.30
Wales	82.14	84.55	85.30
Forth River Basin	81.45	83.51	84.32
Severn River Basin	81.10	84.58	85.67

Table 4.1 *Regional humidity averages 1981 – 2010 (Met Office 2014).*

An RH of 90% within the reaction vessels was deemed likely to promote sample corrosion beyond the error of the oxygen meter to allow corrosion rate characterisation in permitted timescales whilst not representing an unreasonable step up from ambient exterior conditions, especially during the drying phase in wetting/drying atmospheric corrosion cycles.

4.1.3.4 *Protective coatings*

The number of coatings investigated was restricted by cost and time. Sensor spots for oxygen consumption measurements are prohibitively expensive and time to perform measurements is considerable. The number of coatings investigated was limited to three permitting appropriate numbers of coated iron samples and controls to be run.

Coating selection for this research was contextual. With the ubiquity of wrought iron, contexts for coating and criteria for decision-making will be vast in number. Three contextual scenarios have been modelled for this study (Table 4.2).

	Scenario A	**Scenario B**	**Scenario C**
Budget	Large	Medium	Small
Structure (example)	Bridge	Historic gates	Local museum architectural fittings
Rationale	Treatment to engineering standards Thorough surface preparation Industrially recognised coating	Thorough surface preparation Removal of corrosion products to enhance coating performance Conform to historic aesthetic	Limited surface preparation Conform to historic aesthetic Preserve original material Easy to maintain
Expertise	National contractors	Local contractors	Non-specialist
Maintenance	Periodic complete renovation by specialist	Ongoing vigilance and touch up by specialist	Ongoing vigilance and touch up by non-specialist
Coating System	Two-pack epoxy resin primer and intermediate coats Two-pack polyurethane top coat	Single-pack alkyd oil-based primer Single-pack alkyd oil-based top coat	Single-pack, surface tolerant alkyd oil-based coating

Table 4.2 *Contextual scenarios for coating selection.*

A system fitting the criteria of scenario A was recommended by a heritage practitioner and is the same system as applied to the ss Great Britain and other high profile heritage projects. Epoxy resin polymers are commonly used in protective coatings thanks to their desirable properties: good wetting of metal/metal oxide surfaces; good to excellent chemical resistance; easily controlled cross-linking, wide range of molecular weights; ease of forming pigment dispersions; range of available cross-linking reactions; and relatively good water resistance (Bierwagen and Huovinen 2010, 2651). The polyurethane topcoat offers UV resistance to the coating system (Leighs 2008c). Coatings for scenarios B and C were chosen from household name manufacturers and were available off the shelf. Alkyd oil coatings are used extensively because of their low cost and wide range of applications but in an unmodified form are sensitive to hydrolysis (Bierwagen and Huovinen 2010, 2652). Specifics of each coating system are given in 4.3.3, Table 4.4 and Appendix 2 and 3 – 8.

4.2 Investigating the impact of surface preparation method on corrosion of historic wrought iron

4.2.1 Aims and Objectives

This study aims to address the current knowledge gap regarding impact of choice of surface preparation method on effective corrosion prevention for wrought iron by:

- preparing the surfaces of historic wrought iron samples by five methods;
- determining the effect of these preparations on sample surface morphology, retention of existing coatings and corrosion products;
- quantifying the corrosion rates of the samples via measurement of oxygen consumption at high relative humidity;
- relating corrosion rate to surface preparation method.

4.2.2 Characterisation of sample material

The sample material, sourced by Historic Scotland, is a wrought iron railing of unknown provenance (Fig. 4.2). Vestiges of failed coating systems remain on approximately 40-50% of the surface, adhering closely in some areas and loosely in others. Corrosion products also cover the entirety of the railing in the form of closely adhering, coherent oxide layers as well as laminating and powdery corrosion products and pitting.

Figure 4.2 *Iron railing from which sample material was cut.*

Wrought iron is by nature an inhomogeneous material with local compositional differences possible within the same piece of metal (Dillmann et al. 2004; O'Sullivan and Swailes 2009, 260-261; Rawdon 2013). To minimise the chances or extent of compositional variation between the samples they were cut from a continuous length of flat bar iron. However, the skill of wrought ironworkers is such that the bar may have been produced by welding shorter lengths of the metal together without leaving any macroscopically visible indication (Chris Topp heritage blacksmith pers. comm.).

Samples were cut from the wrought iron bar using a hand hacksaw with white spirit as a lubricant to avoid heat from machine sawing. Sample size was 40mm x 30mm x 10mm as dictated by the dimensions of the bar and the diameter of the aperture of the reaction vessel used for the oxygen consumption tests (Fig. 4.3). Each sample was weighed and minor discrepancies in overall dimensions, and hence surface area, were recorded.

Figure 4.3 *Sample of wrought iron railing as cut to form samples.*

Paint layers were examined in profile and elementally analysed using a CamScan Maxim 2040 scanning electron microscope (SEM) equipped with Oxford Instruments energy and wavelength dispersive X-ray spectrometers.

Polished sections of the railing were also analysed using the SEM to determine the composition of the wrought iron. Samples of corrosion products were removed from exposed areas and beneath exfoliating paint and analysed using a PANalytical X'Pert Pro (Cu K_α) X-ray powder diffraction.

4.2.3 Surface preparation methods

Five surface preparation methods, determined through prior testing by Historic Scotland (Wilson et al. 2008), were applied to the historic wrought iron samples:

- airbrasion with glass beads;
- airbrasion with aluminium oxide;
- airbrasion with crushed walnut powder;
- immersion in sodium hydroxide solution followed by wire brushing;
- flame cleaning followed by wire brushing.

Five samples of the wrought iron railing were prepared by each method with five samples left in an as received, untreated condition acting as controls. The methodology used for each preparation method is described below.

4.2.3.1 *Blast cleaning with glass beads, aluminium oxide and crushed walnut abrasive media*

Blast cleaning of samples was carried out using a Texas Airsonics Model AJ-1 airbrasive unit. The airbrasive feed was thoroughly cleaned when changing between abrasive media to avoid cross contamination. The abrasive media were:

- glass beads (Grade No.9 - 44µm; hardness 6 Mohs);
- aluminium oxide (Grade No. 3 - 53µm; hardness 8-9 Mohs);
- crushed walnut shell (Grade No. 6 - 0.3-0.6mm; hardness 3-4 Mohs).

Parameters standardised during the cleaning were:

- pressure - c.4 bar (increased slightly for crushed walnut to due softness of the medium);
- powder flow/aim intensity (5);
- distance of nozzle from sample surface (50mm);
- angle of nozzle to surface (45°);
- end point [aim Sa 2.5 (near white metal)].

Post-cleaning samples were blasted with pressurised air to remove loose blast media from their surfaces.

4.2.3.2 *Immersion in sodium hydroxide followed by wire brushing*

Samples were immersed in a 1.25M solution of sodium hydroxide in deionised water for two hours then rinsed in deionised water until pH 7 was attained in two rinses. Vigorous manual brushing with a stainless steel wire brush removed any remaining coating and loosely adhering corrosion products until there was no further visible change in the sample surface. The samples were then rinsed again in deionised water, blotted to remove excess water and left to dry in a well-ventilated, warm area.

4.2.3.3 *Flame cleaning followed by wire brushing*

A hand held GoSystem Tech Multi Torch MT2055 using propane/butane fuel and having a 17mm burner, a power output of 1000 Watts and a flame temperature of 1350°C was used. A standard protocol for cleaning was developed ensuring samples were exposed to the same part of the flame which was constantly moving across the surfaces. The duration for which each sample was exposed to the flame was similar but with slight variation due to differing amounts of paint and corrosion product adhering to surfaces, as would be the case in practice.

Samples were then brushed vigorously with a stainless steel wire brush until there was no longer any visible change in the surface and blasted with high pressure dry air to remove any remaining loose corrosion products or paint residues.

4.2.3.4 *Determination of end point*

In practice, the end point of surface preparation will be guided by a range of factors. Coating manufacturer instructions may stipulate removal of all oxides and remnants of previous coatings, heritage ethics or aesthetics may prioritise maximum retention of coherent original material and availability of techniques limit possible outcomes. Surfaces would generally be blasted with glass beads and aluminium oxide where the aim was removal of oxides and existing coatings to bare metal (Sa 2.5). This was the end point aimed for here. Crushed walnut having a lower hardness than magnetite limits its use to contexts in which retention of coherent oxides is desirable. A surface free from loosely adherent oxides and vestiges of coating systems was deemed the end point for this technique. Immersion in sodium hydroxide solution and flame cleaning both rely on wire brushing for final removal of loosely adhering corrosion products and are unlikely to remove coherent oxide layers. End point in these cases was when continued brushing caused no further visible change in surface appearance. With all techniques, end point was assessed visually macroscopically as would be the case for their in situ use.

4.2.4 **Examination of resultant surfaces**

Prepared surfaces were subjected to macro and microscopic examination and comparison with untreated control samples. Macroscopic recording was by photography and microscopically by use of a CamScan Maxim 2040 scanning electron microscope (SEM) equipped with Oxford Instruments energy and wavelength dispersive X-ray spectrometers using secondary electron imaging to examine the resultant surface topography. BS EN ISO 8501-1:2007 (British Standards Institute 2007) was used to identify surface preparation grade with respect to the internationally applied standard.

4.2.5 Measuring oxygen consumption and corrosion rates

Samples were individually enclosed within airtight reaction vessels (250ml Mason Ball glass jars with plastic coated brass sealing discs tightened with threaded outer sealing rings of brass which create a seal by deforming a synthetic rubberised ring on the disc) containing 160g silica gel conditioned to 90% relative humidity (RH). Within each vessel was an oxygen sensor spot (World Precision Instruments (WPI) part #503090) adhered to the interior wall of the vessel using silicon adhesive (Radio Spares RTV silicone rubber compound) and a watch glass to separate the sample from the silica gel. The reaction vessels with samples were stored in a Binder KB240 climate chamber to control temperature to 20 ± 0.5°C and avoid RH changes within the vessels which would result from fluctuating temperature. Madgetech RHTemp 101A data loggers monitored the internal environment to ± 3% RH of 28 of the 31 reaction vessels. All vessels maintained humidity between 88 – 93% RH ± 3% (logger error) throughout the test period.

Using a fibre optic probe and WPI OxyMini oxygen meter (WPI OXY-MINI-AOT with cable #501644) the oxygen concentration within each vessel was measured at regular intervals (twice weekly) over an 11 month period (338 days for prepared samples, 257 days for un-cleaned samples). The oxygen within the vessels was replenished by opening the vessel and resealing when internal oxygen pressure became depleted to 150mbar to ensure the reduced partial pressure of oxygen did not influence corrosion rates and samples were photographed at this stage. The precision of the oxygen measurements is 2mbar at atmospheric oxygen pressure of 210mbar and increases proportionally with decreasing oxygen pressure. Control vessels filled with nitrogen showed a negligible ingress of oxygen over a two year period indicating very little leakage of the vessels (Watkinson and Rimmer 2014). A further control vessel containing silica gel, watch glass and sensor spot was measured alongside the sample vessels to quantify the oxygen consumption of the apparatus. This was found to be 0.03 mbar day^{-1} which was subtracted from the oxygen consumption of each vessel when results were analysed.

4.2.6 Examining corrosion rates

The corrosion rate of the samples can be calculated as loss of metal using a simplified equation for corrosion [6] if conversion to a range of oxidation products is not considered. Corrosion is at a constant 90% RH and this offers a continuous film of moisture and unchanging saturation of capillaries, providing a constant barrier. Oxygen diffusion is a likely rate controlling step and the three phase corrosion process involved in wet/dry cycle where the initial phase is the cathodic reaction, reduction of corrosion products (Hoerlé et al. 2004), is unlikely to occur. It is likely that corrosion will more readily equate to the saturated phase of this process where oxygen reduction is the cathode reaction. Analysis of corrosion products may reveal a more complex corrosion outcome but this simplified approach is based on the reasoned estimation that FeOOH predominates.

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH \quad\_\_\_\_\_\_\_\_\_\_\_ \quad [6]$$

This can be related to total loss of the metal, assuming corrosion rate does not change with time, within a calculated number of years in a very humid mid-range temperature environment of 90% and 20°C to provide some *comparative* indication of corrosion rate.

The calculation uses the change in pressure of oxygen in the reaction vessel over the test period (atmospheres), temperature (maintained at 20°C), volume of gas within the reaction vessel (litres) and the gas constant (R = 0.08205746) to calculate the number of moles of oxygen consumed by the corrosion of the sample [15]. The ratio of oxygen moles to iron moles in the corrosion reaction is given in equation [6] and is used to calculate the number of moles of iron converted to FeOOH during the test period by assuming that [6] is the only reaction occurring. Changes to oxidation state of iron in reactive corrosion product phases to balance dissolution of metallic iron can occur immediately after wetting and do not involve oxygen consumption (Stratmann and Hoffmann 1989). This would not be detected by the measurement technique used here but is likely to be insignificant as the samples are constantly at 90%RH. Any contribution from these reactions is not considered in this calculation. The mass of FeOOH per unit area can be calculated [16] and, using the density of iron (7.874 g/cm^3) and, assuming uniform corrosion, the depth of metallic iron becoming FeOOH per unit time can be derived using [17].

- Ideal gas law:

$PV = nRT$ or $n = \frac{PV}{RT}$ ___________ [15]

P = pressure of gas (atm.)
V = volume of the gas (l)
n = amount of substance (moles)
R = ideal gas constant
T = temperature (K)

- Converting mass to moles:

mass = moles x molar mass ___________ [16]

- Calculating depth of iron converted to FeOOH:

depth = mass loss / density of iron ___________ [17]

4.2.7 **Identification of corrosion products**

Following completion of oxygen consumption recording, corrosion products formed on the glass beads, aluminium oxide and flame cleaned samples were mechanically removed and analysed using a PANalytical X’Pert Pro (Cu) X-ray powder diffractometer.

4.2.8 **Flame cleaning**

Reporting the corrosion rates of the prepared and uncoated samples to the sector at the Icon Metals Conference *Amazing Technicoloured Dreamcoats: Protective surface finishes for metals* (November 2013, Wallace Collection) generated consternation amongst practitioners and the laboratory method for flame cleaning was called into question. To address this, samples of gasometer wrought iron (described 4.3.2) were flame cleaned by three different practitioners according to their preferred method for historic wrought iron. Eight samples were prepared by each practitioner. The specifics of their individual flame cleaning methods were recorded for comparison (Table 4.3). All practitioners applied the flame to the surfaces of the samples and intermittently brushed the sample surfaces vigorously with a steel wire brush. Duration of application of the flame to the samples varied between practitioners. The temperature of the flames and the metal were not known by the practitioners; the colour of the metal during cleaning was recorded as an indicator.

Practitioner	*Torch*	*Estimated max. temperature of the metal*	*Metal colour during cleaning*	*Duration of flame application to surface (approx.)*	*Determine end point*
PA	Oxypropane (oxygen cutting boost)	500°C	Dull red	20-30 seconds	Visual cleanliness
PB	Oxypropane (oxygen cutting boost)	100°C	Grey	<10 seconds	Cessation of luminescence of coating and oxide vestiges under flame (Fig. 6.4)
PC	Oxyacetylene (no oxygen boost)	700°C	Cherry red	50-60 seconds	No further corrosion removable or coating visible

Table 4.3 *Parameters of flame cleaning by practitioners.*

Prepared samples were photographed and subjected to the oxygen consumption and corrosion rate measurement method described above. Laboratory flame (method 4.2.3.3) cleaned gasometer sample cross sections were imaged using the SEM in backscatter mode alongside uncleaned gasometer samples to examine impact on oxide layers in section.

4.3 Investigating protective coatings for historic wrought iron

4.3.1 Aims and objectives

This study aims to investigate the effectiveness of commonly applied protective coatings for corrosion prevention of wrought iron by:

- preparing the surfaces of historic wrought iron samples;
- coating the samples with three commonly applied protective coatings (one epoxy resin system and two alkyd oil based coatings);
- quantifying the corrosion rates of the coated samples via measurement of oxygen consumption at high relative humidity;
- relating corrosion rate and practical considerations to a cost benefit analysis of application of these coatings for corrosion prevention of historic wrought iron.

4.3.2 Sample material

Insufficient sample material from surface preparation investigation remained for use in coating system testing. The previous success in standardising historic sample material encouraged further use of historic wrought iron and mid-19th century rolled plate from the Kings Cross/St Pancras gasometer was sourced (courtesy of Pete Meehan).

Optical and scanning electron (CamScan Maxim 2040) microscopy of polished sections confirmed this to be wrought iron due to the presence of stringers of slag. Wavelength dispersive SEM analysis was used to determine the composition of the gasometer metal as part of a separate project run jointly with Eric Nordgren. XRD analysis of the corrosion products present using a PANalytical X'Pert Pro (Cu K_α) X-ray powder diffraction identified magnetite, goethite and lepidocrocite, (Figs 5.31-5.33). This is consistent with corrosion products reported on iron subjected to atmospheric corrosion (Bouchar et al., 2013).

The large gasometer plates are a consistent thickness (4mm). Samples were cut (to 30mmx40mm) from one plate by a contractor using a water cooled cutting process to minimise the temperature increase and associated changes in the microstructure of the wrought iron. Historic wrought iron is by nature an inhomogeneous material (Dillmann et al. 2004) and local differences in microstructure and slag distribution are possible. Samples were cut from the same plate to minimise compositional variation. Possible removal of chlorides by cooling water was not considered problematic for this investigation.

4.3.3 Protective coatings

Focus was on the performance of an epoxy resin system (System A) such as has been used in high profile, big budget conservation projects (e.g. ss Great Britain, Forth Rail Bridge) against that of a low cost, widely available, household name, alkyd oil-based system (System B). A context in which the facilities for more extensive surface preparation are not available is modelled using a surface tolerant alkyd oil-based coating from the same household name manufacturer (Coating C). A summary of the coatings is given in Table 4.4 and further details of the coatings and their application requirements in Appendix 2.

Manufacturer	***Identifier***	***Coating***	***Trade Name***	***Chemistry***
Leighs	System A	Primer	Metagard L574	Two-pack epoxy
		Primer/ build	Epigrip C400V3	Two-pack epoxy – zinc rich
		Topcoat	Resistex C137V2	Two-pack acrylic polyurethane
Hammerite	System B	Primer	Red Oxide Primer	Oil-based
		Topcoat	Garage Door	Alkyd oil-based
	Coating C	Single coat system	Direct to Rust Metal Paint	Alkyd oil-based

Table 4.4 *Overview of coatings investigated.*

4.3.4 Sample surface preparation

Samples were prepared according to coating manufacturer recommendations and in line with the findings from surface preparation testing in this investigation. System A and B samples were blasted to Sa2.5 using aluminium oxide powder. The method for blasting was as detailed above (4.2.3.1). Coating C is surface tolerant (suitable for application over existing corrosion products) hence surface preparation was limited to wire brushing to remove non adherent corrosion products. End point of wire brushing was when no more loose corrosion product was removed. For images of prepared and coated samples see Figure 5.34.

4.3.5 Coating application

Coating systems were applied as per manufacturer recommendations for brush application. Brush application was chosen as the most readily available method and because of suggestions that brush application leads to the most effective adhesion of coating to substrate (various practitioners *pers. comm.*). Numbers of applications of each coating were as recommended for optimal performance of the overall system in each case. Over-coating intervals were in line with those specified by the manufacturers given the curing conditions of 22-24^{o}C and 45-50% RH. A full summary of application details from the manufacturer data sheets is given in Appendix 2. Application was with a 1” Harris synthetic brush, as appropriate for the size of the samples, with numbers of strokes determined by viscosity and wetting properties of the coatings. Application aimed to cover the entirety of the sample, minimising the appearance of holidays and brush marks. Curing conditions were interior and relatively constant at c.24°C and 45% RH with air extraction.

4.3.6 Oxygen consumption and corrosion rates

The prepared samples and controls were subject to the oxygen consumption and corrosion rate quantification method described above (4.2.5). Measurements of oxygen within the vessels were conducted at regular intervals (approximately every 14 days) over a period of 540 days.

4.3.7 Control samples

Changing the sample material necessitated determination of baseline oxygen consumption of control samples to allow comparison of corrosion rate and assessment of standardisation. Blasted and wire brushed samples were prepared to provide background consumption levels for substrates of Systems A/B and Coating C respectively.

The coating systems themselves were likely to consume oxygen during the corrosion testing. In order to subtract the oxygen consumption of the coating systems from the overall oxygen consumption, giving that of the metal substrate only, the coatings were also applied to inert substrates (glass) of the same surface area as the iron samples. These were then exposed to the same controlled environment and oxygen consumption measurement procedure. The oxygen consumption of a control vessel containing silica gel, watchglass and glass slide was also recorded.

4.3.8 Practical observations

The requirement to approach evaluation of the coating systems pragmatically calls for consideration of the practicalities of their application. During the coating process relevant observations were made regarding the properties of the coatings, their behaviour and any factors which might affect application in the field.

4.3.9 **Properties of cured coatings**

Coatings were assessed following the curing period for visible holidays, brushstrokes, run back from edges, tack and aesthetics. These properties may affect performance and suitability of a coating for application to historic material.

4.3.9.1 *Dry film thicknesses*

Recommended dry film thickness (DFT) values are specified by the manufacturers for each coating for optimum performance and aim to strike a balance between slumping caused by application of too great a mass of coating and holidays and lack of coverage from too little. DFT is argued to be the most important single measurement made during application and inspection of protective coatings as these are designed for optimum performance when applied within a narrow range of DFT as specified by the manufacturer (DeFelsko 2014, 5). These values vary for different application methods and can directly impact physical properties of the coatings. Following curing of test samples coated with systems A and B and coating C, the dry film thicknesses were tested using a DeFelsko PosiTector 6000 equipped with a Ferrous/Non-Ferrous substrate probe calibrated on uncoated substrate material using standard calibration shims 10371F, 8944F and 8623F accurate to ±0.43μm. In its ferrous substrate function the probe uses the magnetic principle to measure the thickness of non-magnetic coatings applied to ferrous metals with an error of ±1.0μm at DFT 0-50μm and ± 2.0μm at DFT >50μm (DeFelsko 2014, 3).

4.3.9.2 *Coating adhesion*

Effective adhesion of the coating to the substrate is a parameter for success of protective coatings. It was measured for each coating using a DeFelsko PosiTest AT-A Automatic Adhesion Tester as per the manufacturer instructions (DeFelsko 2011). Aluminium pull-off dolly surfaces were prepared by rubbing the base of each dolly 5 times across a 3M Scotch-Brite TM General Purpose Hand Pad 7447. Any residue from this abrasion was removed by wiping with a clean cloth. The surface of the coating was also prepared by passing the same abrasive pad across the surface 5 times and degreasing with industrial methylated spirits. Prior testing revealed no negative effects of this small amount of alcohol on the coatings. 10 dollies per coating system were adhered to the coated samples using Loctite Universal Superglue applied in a uniform film to the dolly base, the dollies pressed onto the coated surface for 40 seconds and excess adhesive wiped from around the dolly sides. The adhesive was allowed to cure for 24 hours before the pull-off test was carried out. The cyanoacrylate superglue was selected as an adhesive due to their use in the field where a quick-curing adhesive allows pull-off testing to be achieved in a short time.

5 Results

5.1 Investigating the impact of surface preparation method on corrosion of historic wrought iron

5.1.1 Railing sample characterisation

The mean composition of the sample analysed was 99% iron, 0.37% silicon, 0.36% phosphorus and 0.27% manganese (Table 5.1) which is typical of a wrought iron. Slag content was moderate and relatively evenly distributed in stringers, although inclusions varied in size from <10µm to >600µm (Figs 5.1, 5.2). Corrosion was localised and pitting was present (Fig. 4.3). XRD identified goethite (αFeO(OH) diffraction code 01-081-0462), magnetite (Fe_3O_4 diffraction code 01-085-1436) and lepidocrocite (γFeO(OH) diffraction code 01-074-1877) to be present as corrosion products (Fig. 5.3). There were at least nine layers of paint on the samples and the compositions of these (Figs 5.4-5.8) indicated the presence of lead based coatings, those with barium sulphate fillers, cobalt drying agents, copper based pigments and a suggestion of zinc. Overall the picture is of an ad hoc painting maintenance regime with a range of pigment and paint types such as might be expected in the protective coating of an outdoor railing.

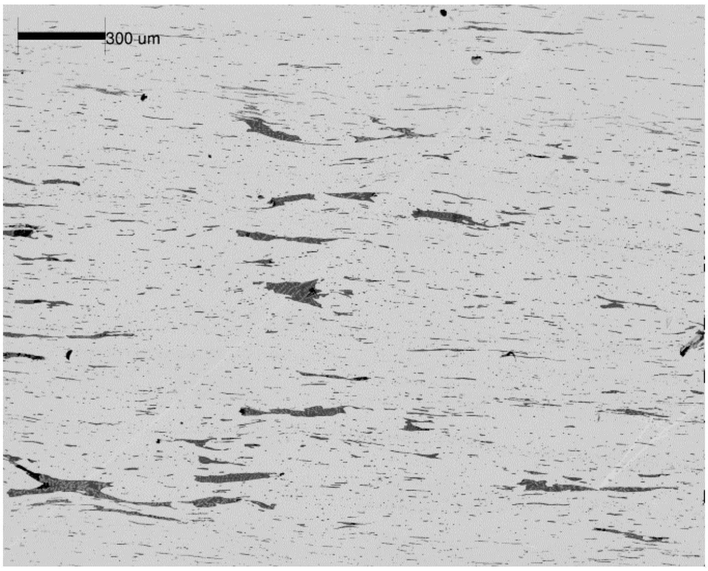


Figure 5.1 *SEM image of polished section of railing wrought iron showing slag inclusions distributed in direction of rolling.*

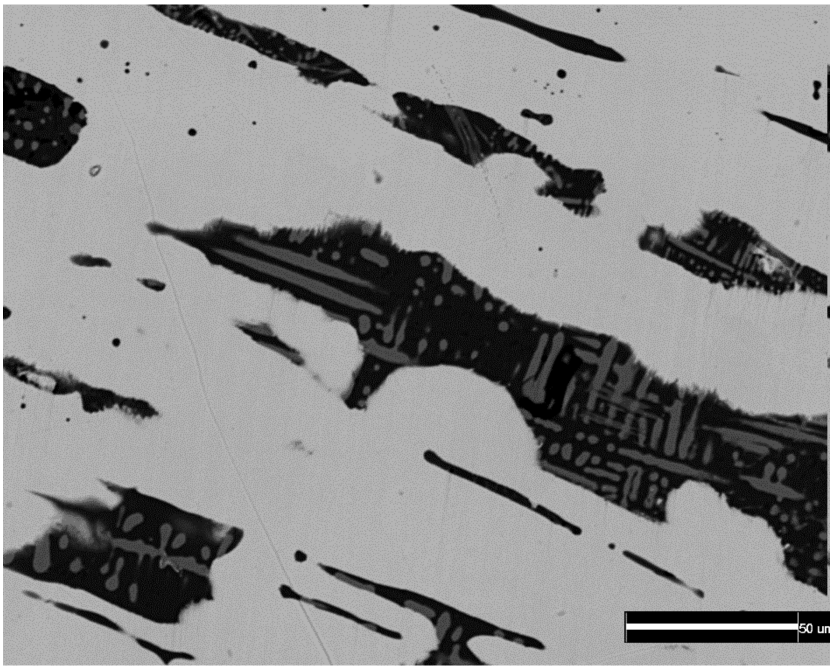


Figure 5.2 *Backscatter electron SEM image showing detail of two phase slag inclusions with typically rounded wüstite (FeO).*

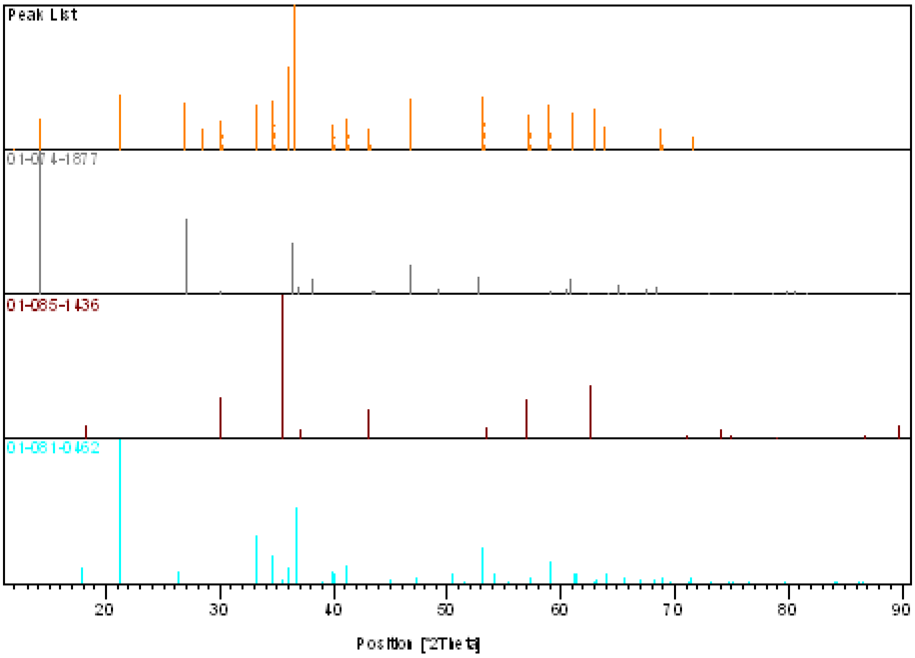


Figure 5.3 *Diffraction patterns of corrosion sample and matching compounds (top to bottom): the corrosion product sample; lepidocrocite (01-074-1877); magnetite (01-085-1436); goethite (01-081-0462).*

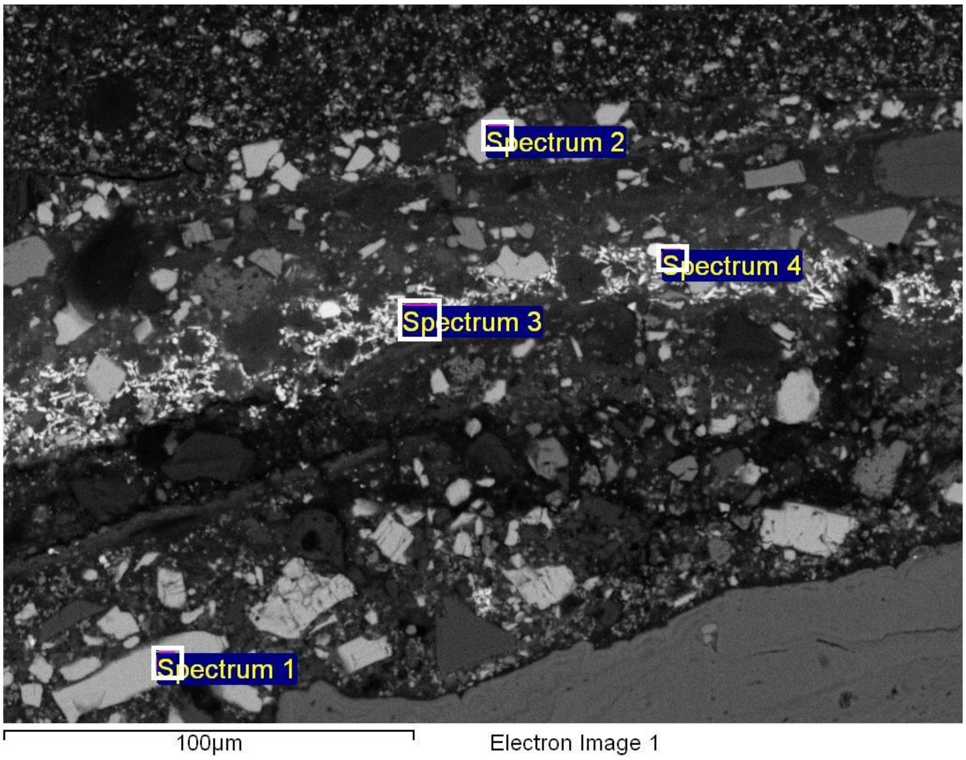


Figure 5.4 *Backscattered electron image showing location (indicated by white squares) of analyses of paint layers (aim to analyse pigment inclusions) from the sample material. Spectra 1-4 are given (Figs 5.5-5.8).*

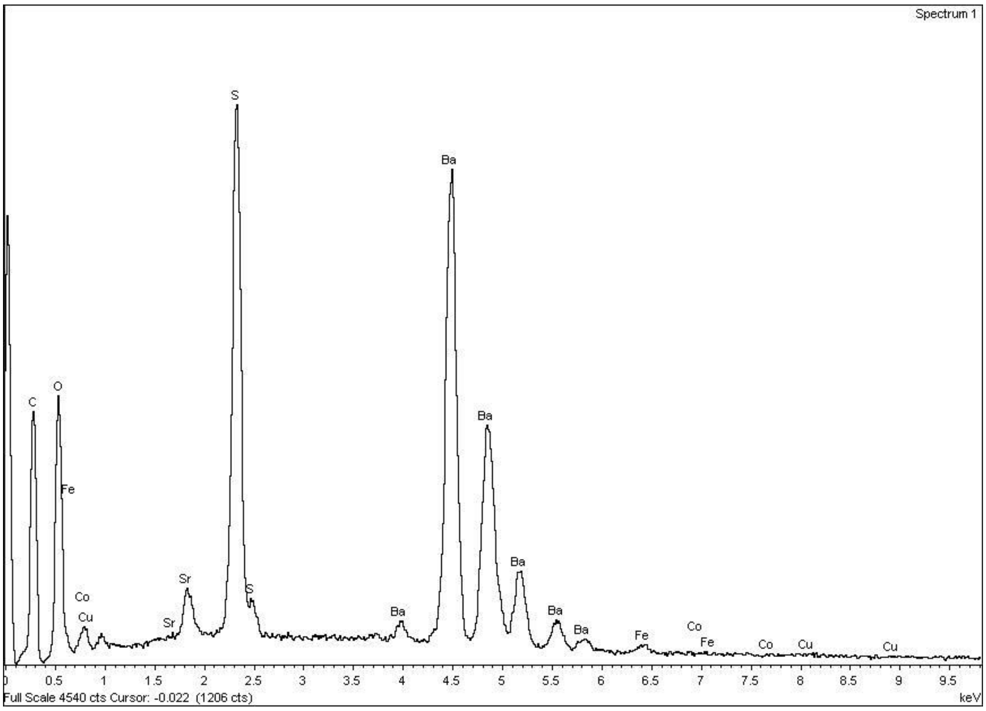


Figure 5.5 *Spectrum 1 of SEM analysis of paint layers on sample material (location indicated in Fig. 5.4) showing major peaks for sulfur, and barium with minor peaks for copper, cobalt, strontium and iron.*

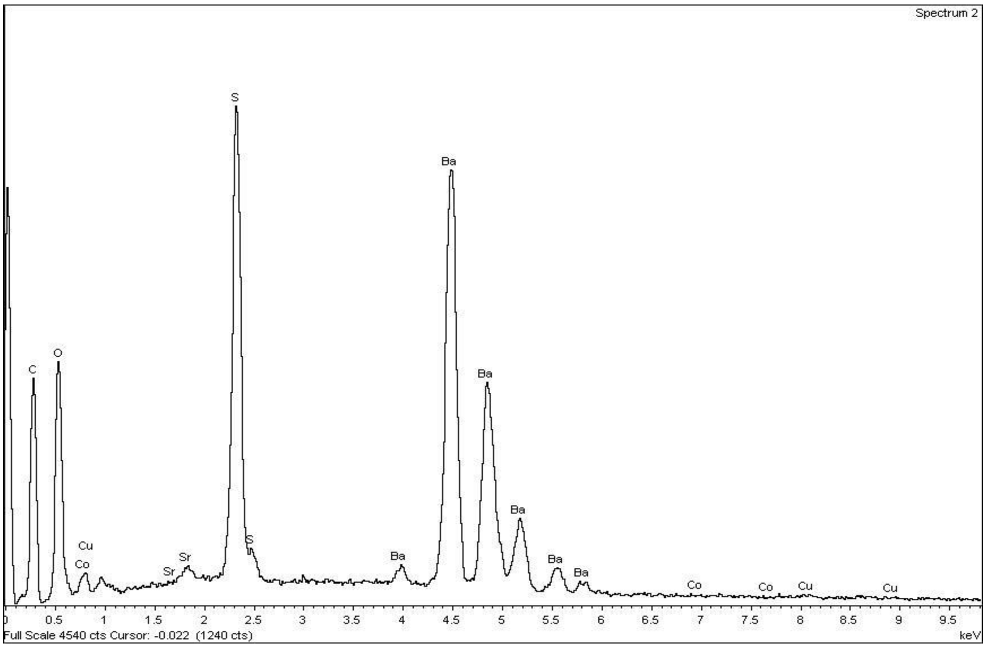


Figure 5.6 *Spectrum 2 of SEM analysis of paint layers on sample material (location indicated in Fig. 5.4) showing major peaks for sulfur and barium and minor peaks for copper, cobalt and strontium.*

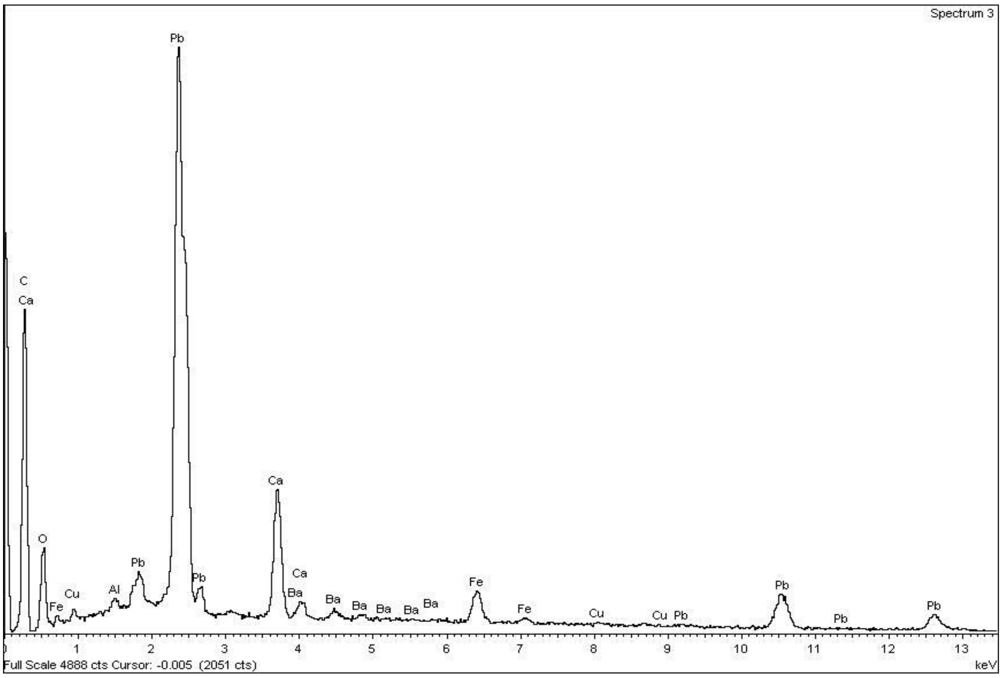


Figure 5.7 *Spectrum 3 of SEM analysis of paint layers on sample material (location indicated in Fig. 5.4) showing major peaks for lead and calcium and minor peaks for aluminium, barium and copper.*

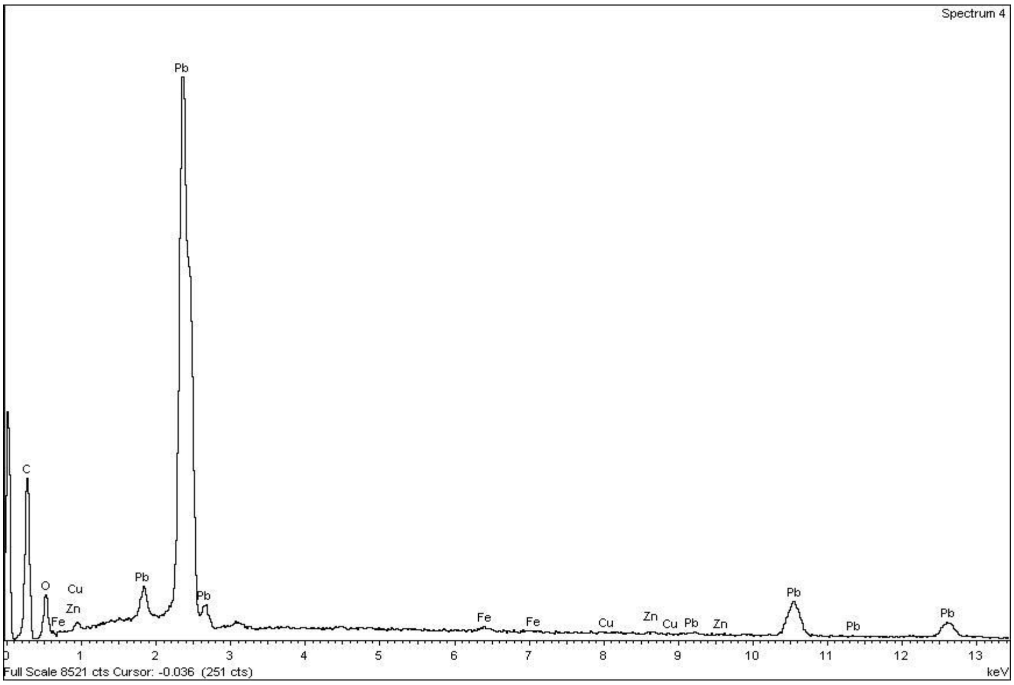


Figure 5.8 *Spectrum 4 of SEM analysis of paint layers on sample material (location indicated in Fig. 5.4) showing major peaks for lead and minor peaks for copper, zinc and iron.*

	Weight %				
	Si	**P**	**Mn**	**Fe**	**Total**
Spectrum 1	0.4	0.3	0.28	99.02	100
Spectrum 2	0.36	0.41	0.33	98.91	100
Spectrum 3	0.36	0.36	0.21	99.06	100
Mean	0.37	0.36	0.27	99	100
Std. deviation	0.02	0.05	0.06	0.08	
Max.	0.4	0.41	0.33	99.06	
Min.	0.36	0.3	0.21	98.91	

Table 5.1 *Results of SEM analysis of the wrought iron giving compositions of three areas analysed.*

5.1.2 Preparation of surfaces

The results of cleaning (Fig. 5.9) reflect the end point goals and limitations of the methods employed as discussed above. Both aluminium oxide powder and glass beads blasting exposed the entire metal surface. Crushed walnut blasted, sodium hydroxide immersed and flame cleaned surfaces were visually similar in their retention of oxides but differed in colour and extent of powdery corrosion products evident.

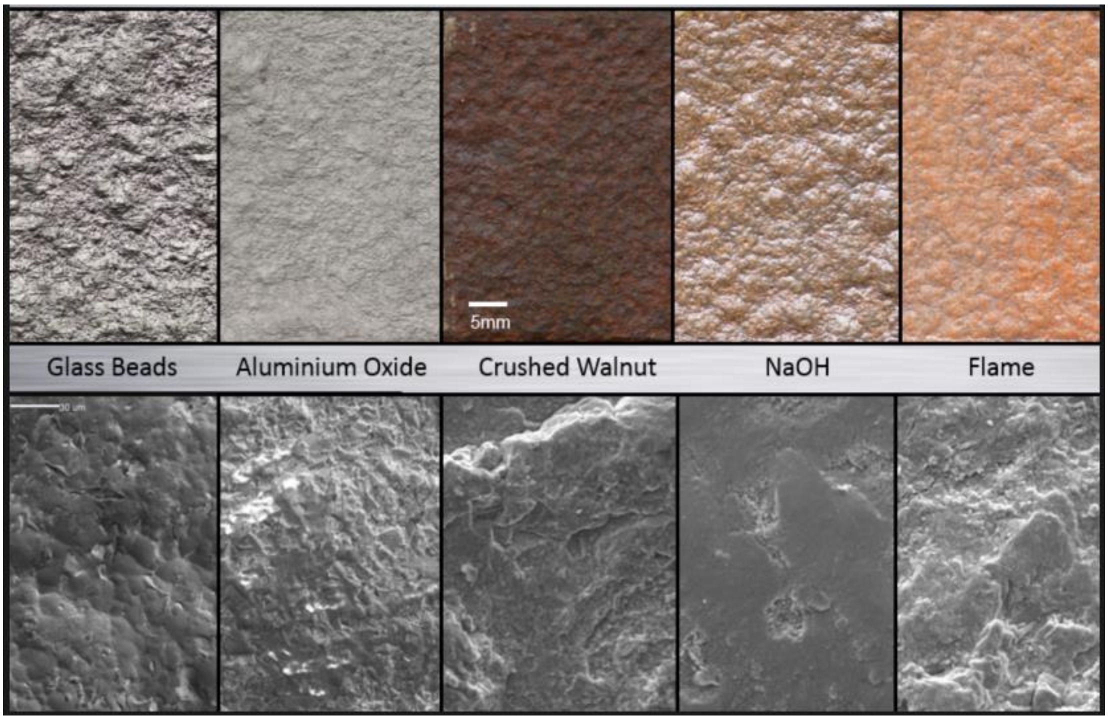


Figure 5.9 *Morphology of metal surface post-preparation shown in macroscopic (upper) and secondary electron SEM (lower) images for each surface preparation method.*

Preparation Method	**Coherent oxide layer**	**Powdery corrosion products**	**Micro-cracks in oxide**	**Surface profile**	**Corresponding surface preparation grade (BS EN ISO 8501-1:2007)**
Un-cleaned control	Yes	Yes	No	Rough	Rust Grade D
Glass beads blasting	No	No	N/A	Undulating	D Sa 2.5
Aluminium oxide blasting	No	No	N/A	Rough	D Sa 2.5
Crushed walnut blasting	Yes	No	No	Rough (ice floes)	D Sa 1
Sodium hydroxide/ wire brushing	Yes	No	No	Smooth	D St 1
Flame cleaning/ wire brushing	Yes	Yes	Yes	Rough (ice floes)	Fl (approx.)

Table 5.2 *Classification of surface preparation outcomes using BS EN ISO 8501-1:2007 (British Standards Institute 2007).*

5.1.3 Oxygen consumption and corrosion rates of prepared samples

All samples within all preparation methods, including the unprepared controls, consumed oxygen during the 350 days of testing (Figs 5.10-5.15). The rates of consumption differed according to the preparation technique used but patterns of consumption are similar; an initial fast phase followed by a steady rate. While the range of oxygen consumption rates within a treatment likely reflects the difficulty of standardisation and reproducibility for the heritage metal samples, patterns emerge for oxygen consumption according to preparation method (Figs 5.16, 5.18). Oxygen consumption is given as a function of surface area (Fig. 5.18, Table 5.3) but it should be noted that surfaces are not perfectly planar and variation in surface morphology is inherent in the preparation methods (Figs 4.3, 5.9). Flame and wire brush cleaning, aluminium oxide blasting and glass beads blasting have averages that are faster than the untreated control samples, whereas both crushed walnut blasting and sodium hydroxide and wire brush preparations are significantly slower than the untreated samples. Oxygen consumption values are used to calculate moles of iron theoretically reacting to form corrosion products (Table 5.3) in accordance with the methodology discussed in 4.2.6. It is possible to calculate the corresponding loss of depth of metallic iron across sample surfaces but this is not appropriate for the localised corrosion seen on these samples (Fig. 5.19).

The data demonstrates broad agreement within preparation methods, except for two anomalous results; aluminium oxide blasting (HS7) and flame cleaning (HS25) (Figs 5.10-5.15). Statistically significant differences between corrosion rates of sodium hydroxide immersed and aluminium oxide blasted samples, sodium hydroxide immersed and flame cleaned samples and crushed walnut blasted and flame cleaned samples (Table 5.4).

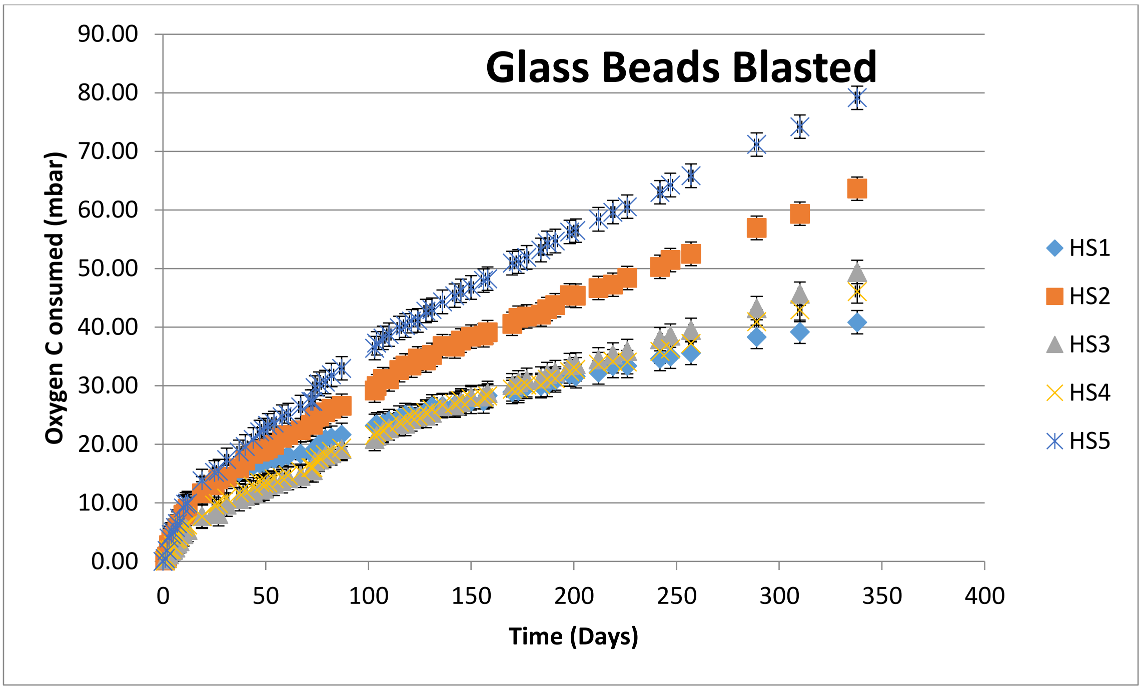


Figure 5.10 *Oxygen consumption of glass beads blasted samples at 90% RH.*

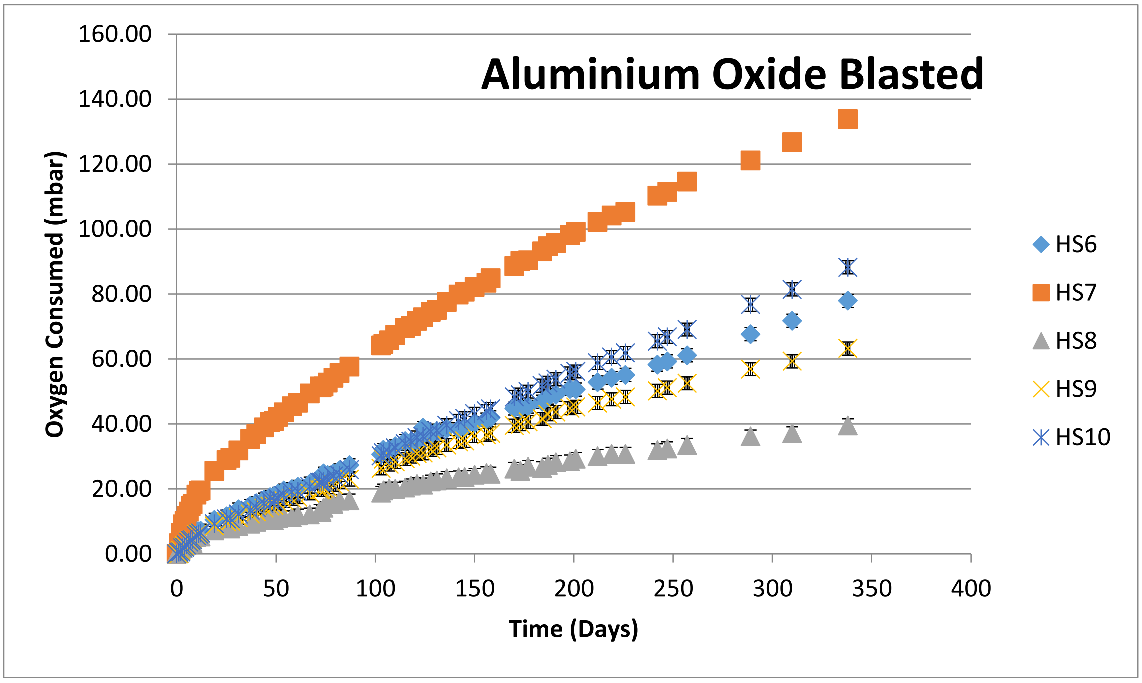


Figure 5.11 *Oxygen consumption of aluminium oxide blasted samples at 90% RH.*

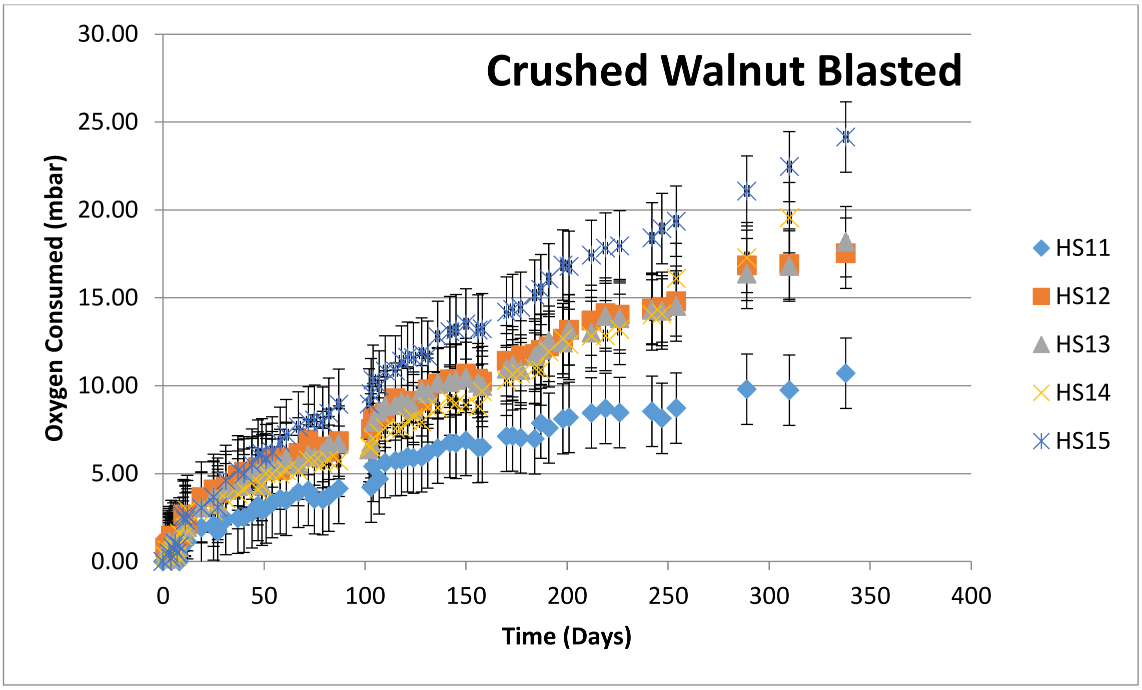


Figure 5.12 *Oxygen consumption of crushed walnut blasted samples at 90% RH.*

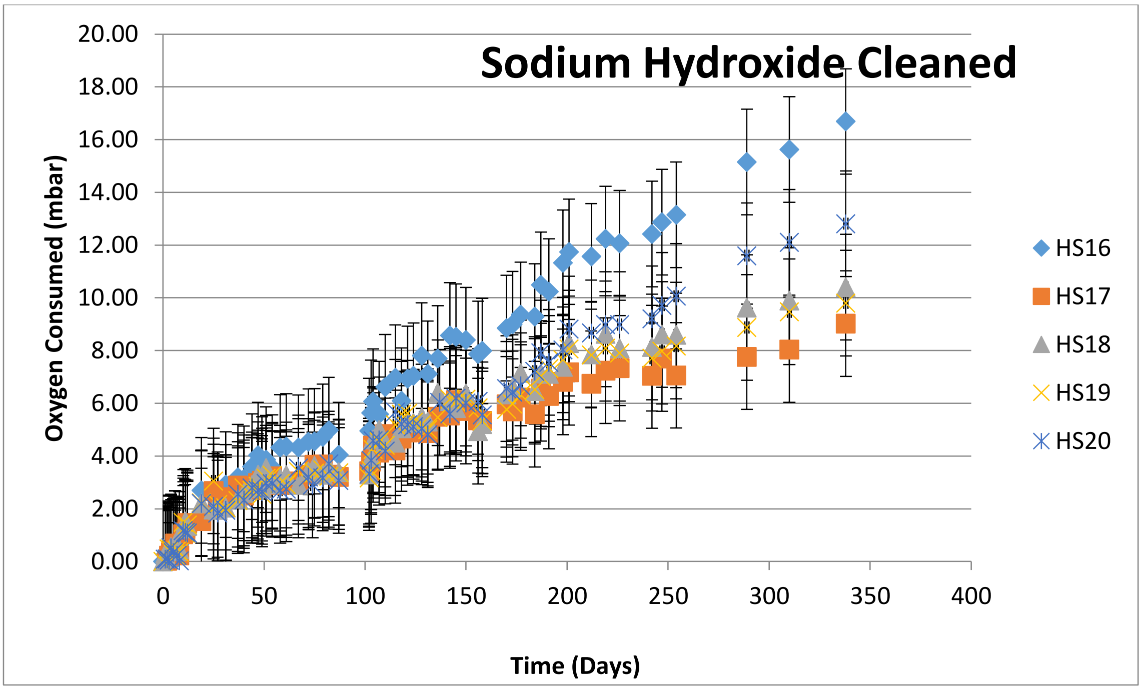


Figure 5.13 *Oxygen consumptiom of sodium hydroxide and wire brush cleaned samples at 90% RH.*

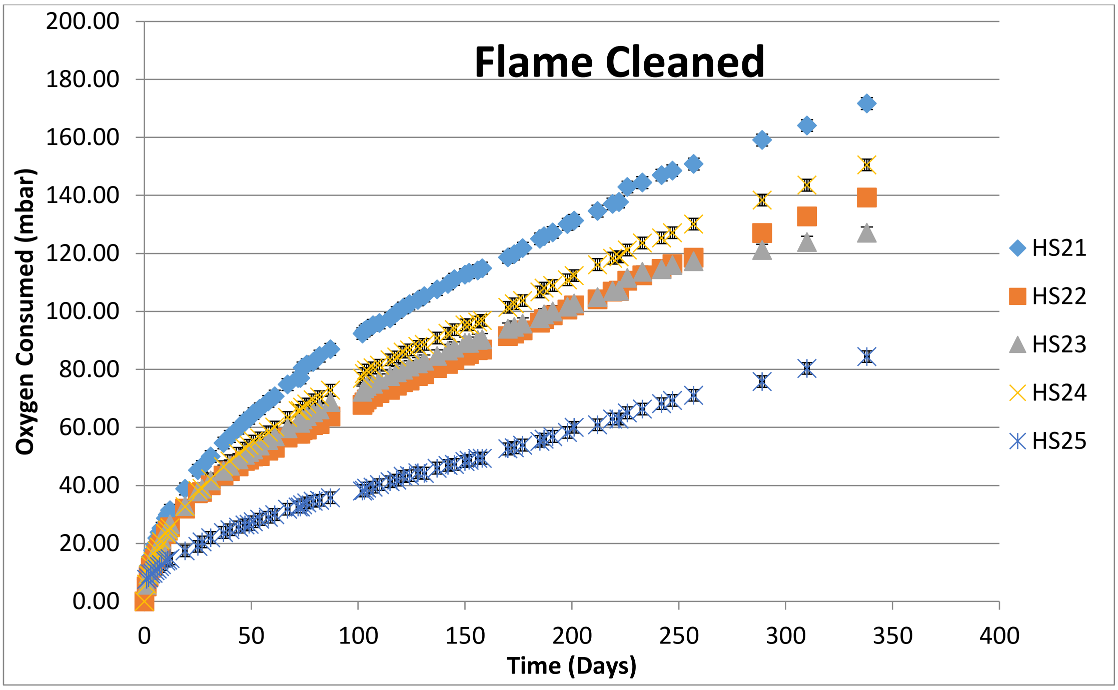


Figure 5.14 Oxygen consumption of flame and wire brush cleaned samples at 90%RH.

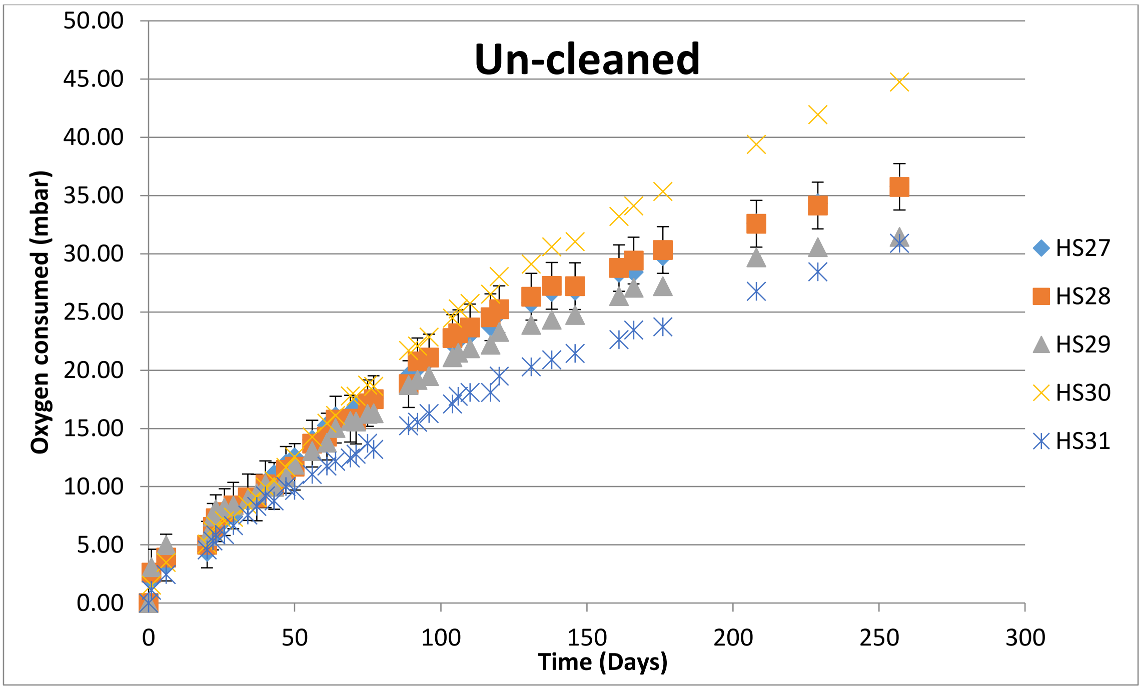


Figure 5.15 *Oxygen consumption of un-cleaned railing samples at 90% RH.*

Prep Method	**Sample**	**O_2 Consumption** (mol/year/mm^{2}x10^{-8})	**Average O_2 Consumption** (mol/year/mm^2 x10^{-8})	**Fe Converted to FeOOH** (mol/year/mm^2 x10^{-8})	**Average Fe Converted to FeOOH** (mol/year/mm^2 x10^{-8})
Glass Beads	HS1	7.76	10.58	10.35	14.11
	HS2	12.16		16.22	
	HS3	9.16		12.22	
	HS4	8.90		11.87	
	HS5	14.93		19.91	
Aluminium Oxide	HS6	15.14	15.58 (12.84 without anomalous result)	20.18	20.77 (17.11 without anomalous result)
	HS7	26.54		35.38	
	HS8	7.64		10.19	
	HS9	12.09		16.12	
	HS10	16.47		21.97	
Crushed Walnut	HS11	1.94	3.06	2.58	4.08
	HS12	3.18		4.24	
	HS13	3.03		4.04	
	HS14	3.17		4.22	
	HS15	3.98		5.31	
Sodium Hydroxide	HS16	3.00	2.16	4.00	2.89
	HS17	1.67		2.23	
	HS18	1.96		2.61	
	HS19	1.90		2.53	
	HS20	2.29		3.05	
Flame	HS21	33.16	26.03 (28.48 without anomalous result)	44.21	34.70 (37.97 without anomalous result)
	HS22	26.30		35.06	
	HS23	24.86		33.15	
	HS24	29.60		39.47	
	HS25	16.21		21.61	
Un-cleaned	HS27	6.66	6.70	8.88	8.94
	HS28	6.57		8.76	
	HS29	5.93		7.91	
	HS30	8.06		10.75	
	HS31	6.30		8.40	

Table 5.3 *Oxygen consumption averaged over test period (mol/year/mm^{2}x10^{-8}) and theoretical conversion of metallic iron to FeOOH (mol/year/mm^{2}x10^{-8}) of all samples giving averages by preparation method. All consumption values are given with consumption of the control vessel (set up without sample) removed. Calculations of metallic iron conversion assume that all oxygen consumed reacts directly with metallic iron to form FeOOH and as such is an estimate of the iron consumed since some oxygen will be involved in redox reactions within the corrosion process.*

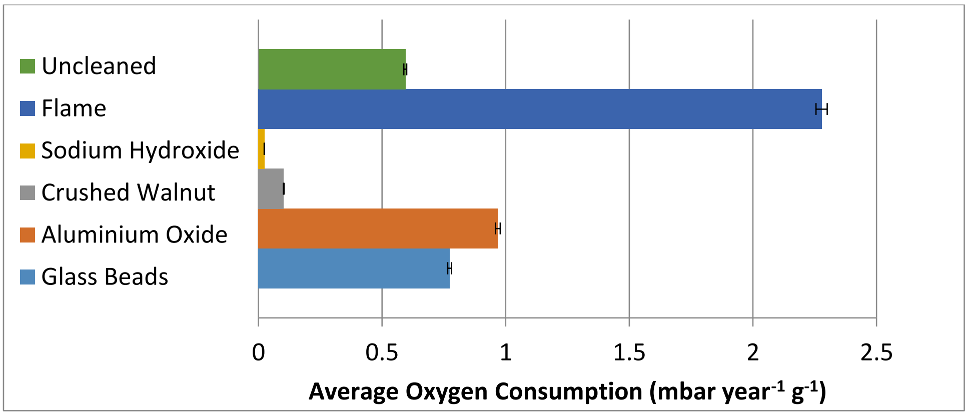


Figure 5.16 *Average oxygen consumption of samples prepared by each preparation method and control samples. The consuption of the control vessel without sample has been subtracted and the anomalous result for aluminium oxide and flame cleaned samples.*

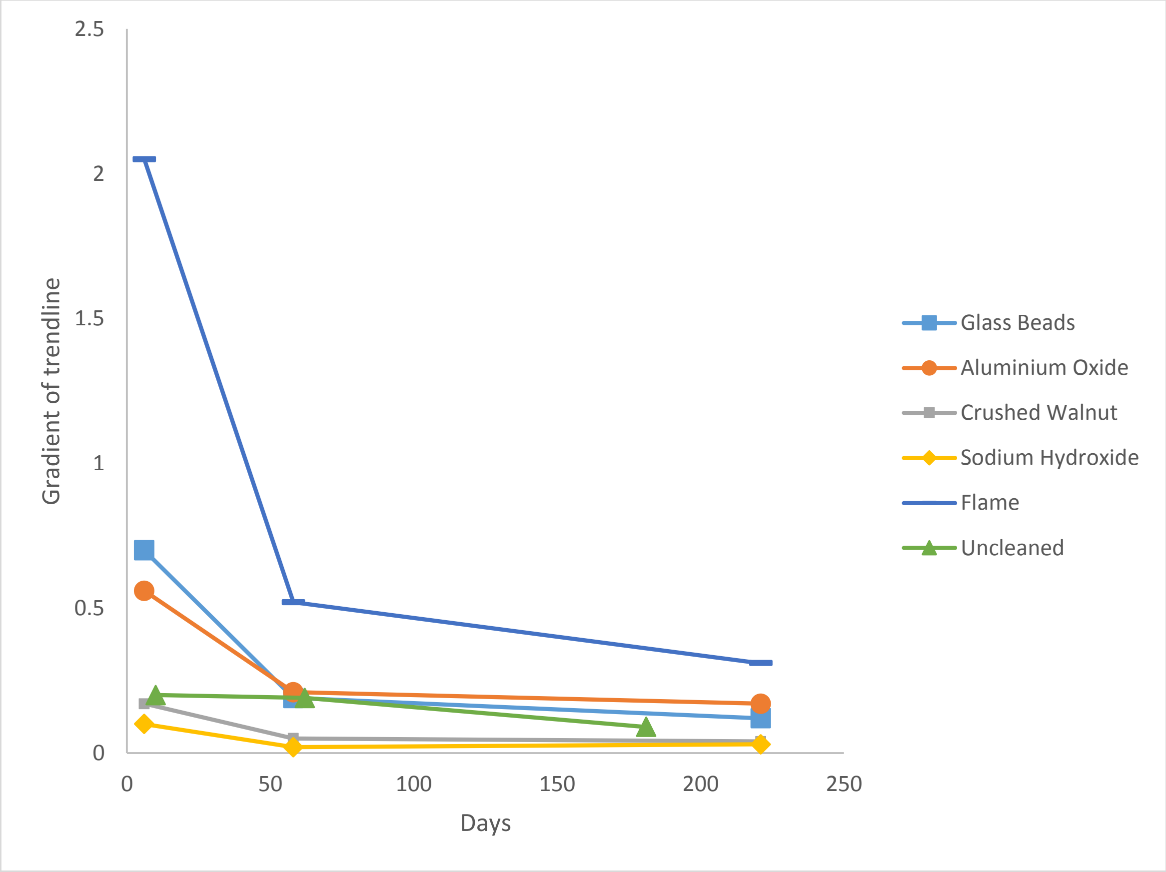


Figure 5.17 *Change in gradient of trendline (i.e. rate) for average oxygen consumption of samples by surface preparation method. Points denote midpoint of gradient period.*

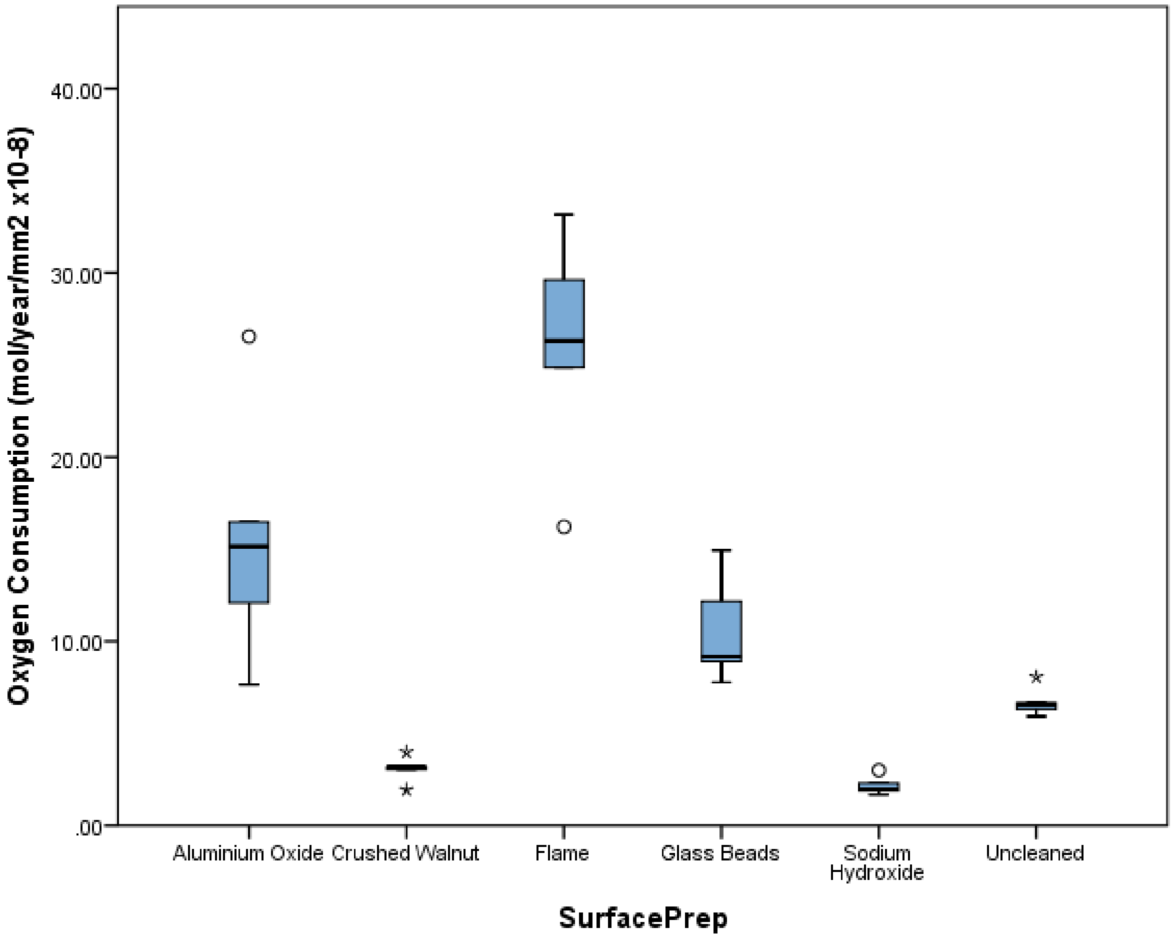


Figure 5.18 *Boxplot showing oxygen consumed by samples prepared by each method (mol/year/mm^2 x 10^{-8}) as averaged over test period. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

Significantly different oxygen consumption (mol/year/mm^2)
Sodium Hydroxide / Aluminium Oxide
Sodium Hydroxide / Flame
Crushed Walnut / Flame

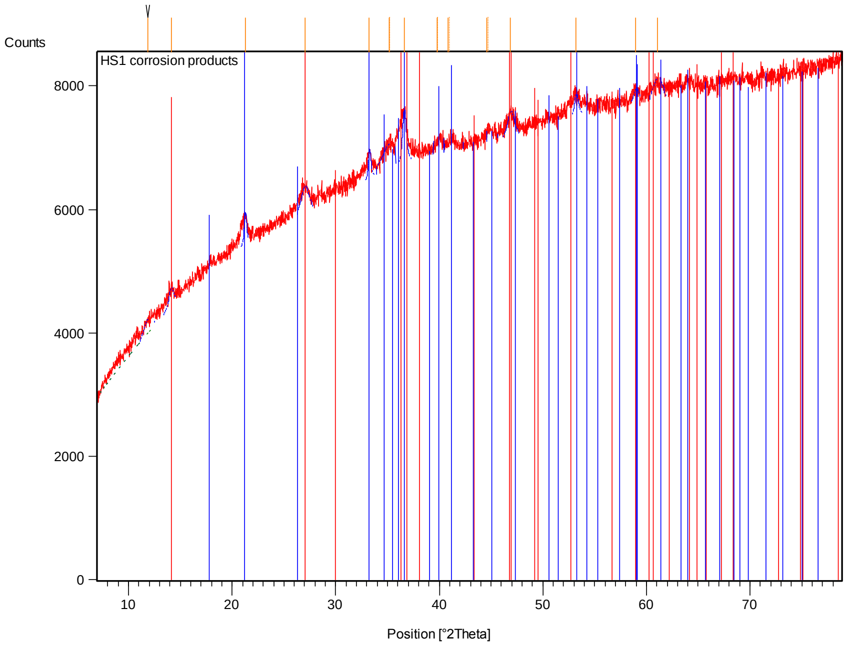
Table 5.4 *Significantly different oxygen consumption per year per mm^2 of iron between surface preparation methods (calculated by Kruskal-Wallis and with a significance level of 0.05). Sodium Hydroxide / Glass Beads and Flame / Uncleaned results are close to significantly different but do not fall within the 0.05 significance level.*

5.1.4 Visual sample surfaces post high RH environment

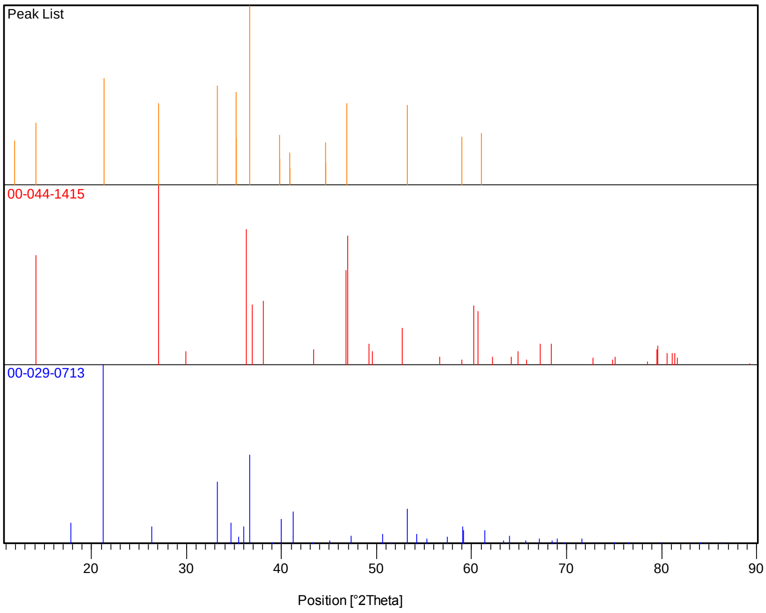
Figure 5.19 *Comparison of prepared and post-high RH exposure surfaces. Images show sample surfaces of 30mm x 40mm.*

5.1.5 XRD of corrosion products formed during high RH exposure

All samples subjected to 90% relative humidity testing developed fresh corrosion products on their surfaces during the oxygen consumption tests (Fig. 5.19). XRD analysis of samples of the fresh corrosion product identified goethite and lepidocrocite for all preparation methods and controls except flame cleaning (Figs 5.20 and 5.21). Both goethite and lepidocrocite are products commensurate with corrosion in the atmosphere (Santarini 2007, 29) while hematite is expected at high temperature either as a transformation product or as a newly formed corrosion product (Cornell and Schwertmann 2003). Chloride contamination of samples is thought to be low as evidenced by an absence of akaganeite in the analysis (Réguer et al. 2007; Zucci et al. 1977).

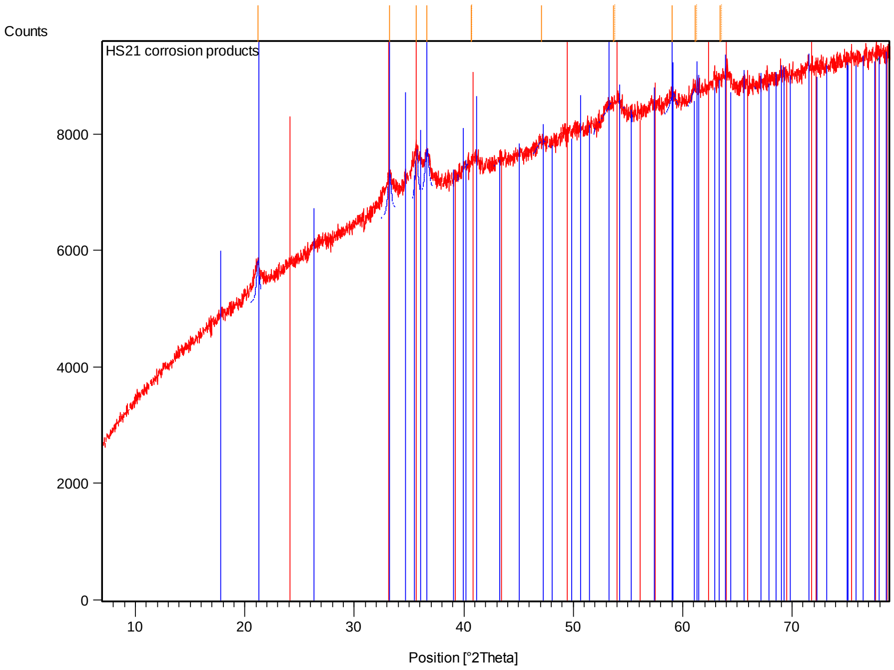


a)

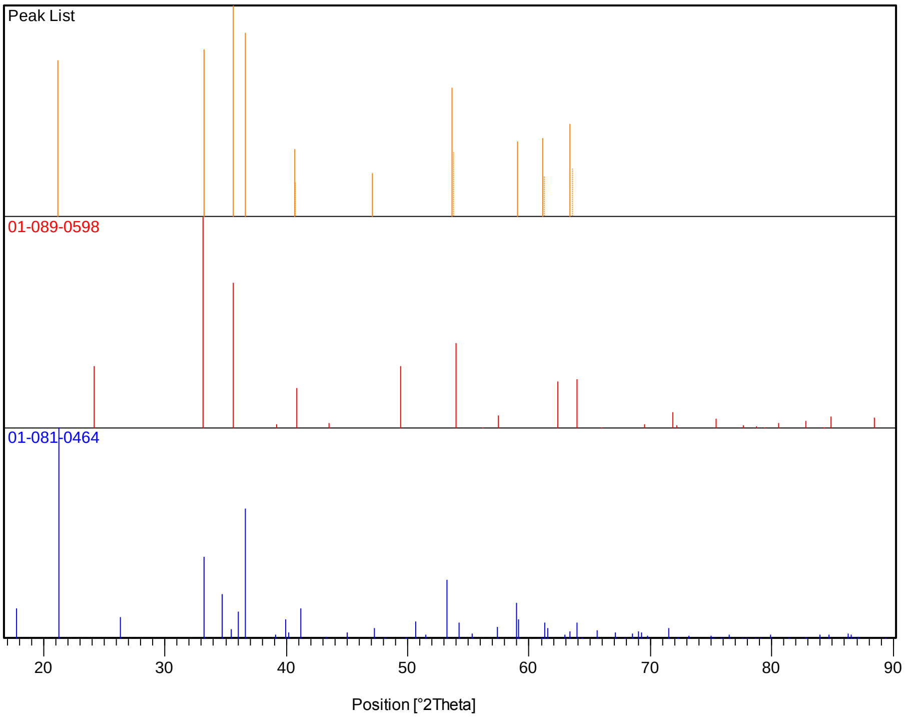


b)

Figure 5.20 a) *Diffractogram of corrosion products from glass beads cleaned sample;* ***b)*** *patterns of identified corrosion products (uppermost pattern) indicating presence of lepidocrocite (00-044-1415 (middle pattern)) and goethite (00-029-0713 (lowest pattern)).*



a)



b)

Figure 5.21 a) *Diffractogram of corrosion products from flame cleaned sample;* ***b)*** *patterns of identified corrosion products (uppermost pattern) indicating presence of hematite (01-089-0598 (middle pattern)) and goethite (01-081-0464 (lowest pattern)).*

5.1.6 **Practitioner flame cleaned samples**

5.1.6.1 *Oxygen consumption*

All the practitioner flame cleaned samples consumed oxygen within the test period. All (Figs 5.22-5.24) show the same general trend of fast initial consumption rate and then a slowing down evidenced by the levelling off of the consumption graphs similar to the laboratory prepared samples (Fig. 5.14). Use of different sample material precludes direct comparison of laboratory and practitioner flame cleaned samples. When compared to Sa2.5 aluminium oxide blasted samples and wire brushed samples of the same gasometer material (Figs 5.25, 5.26), the Practitioner C (PC) corrosion rate is very similar to the wire brushed substrate but Practitioner A (PA) and Practitioner B (PB) are significantly higher.

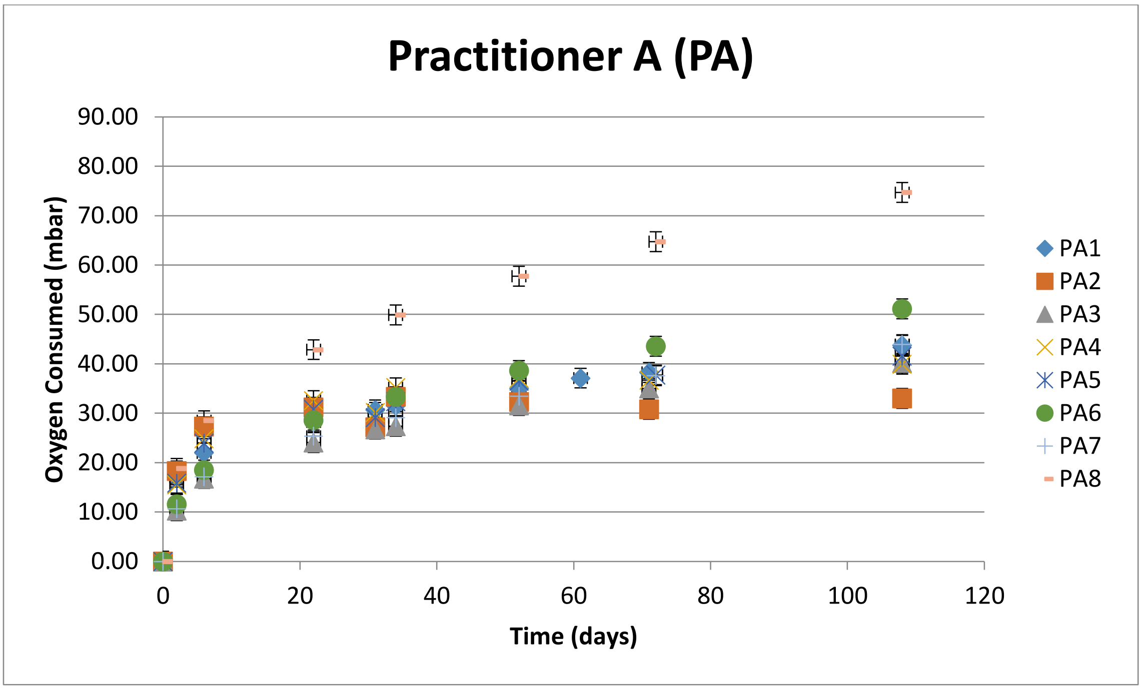


Figure 5.22 *Oxygen consumption of samples flame cleaned by Practitioner A and subsequently exposed to 90% RH.*

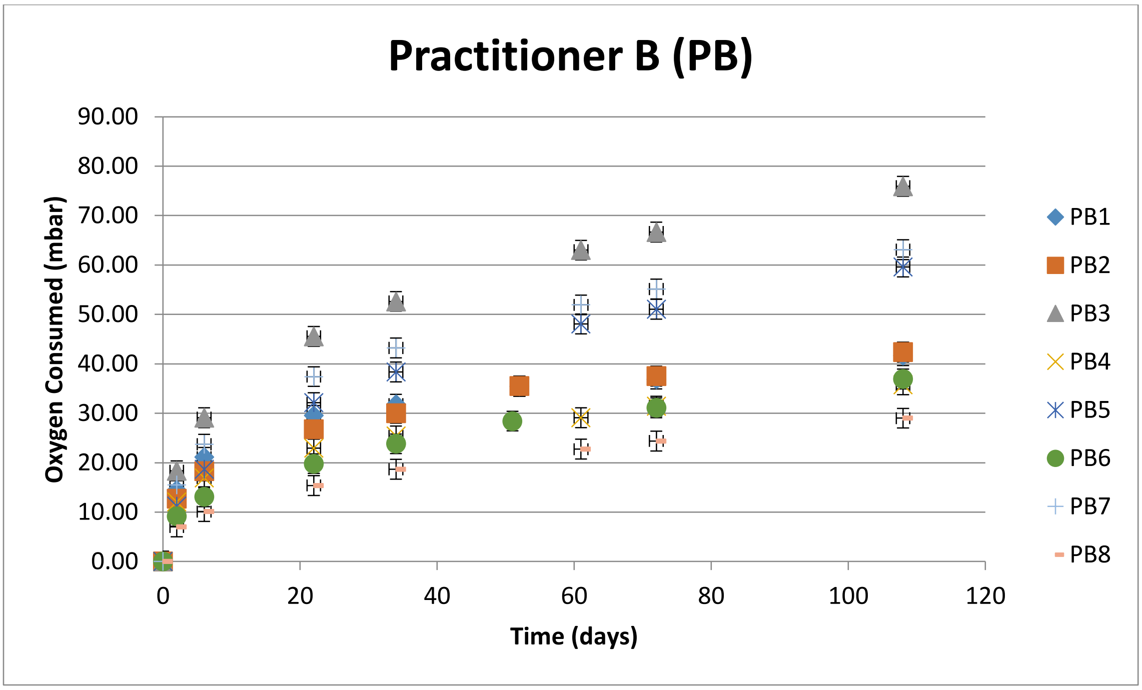


Figure 5.23 *Oxygen consumption of samples flame cleaned by Practitioner B and subsequently exposed to 90% RH.*

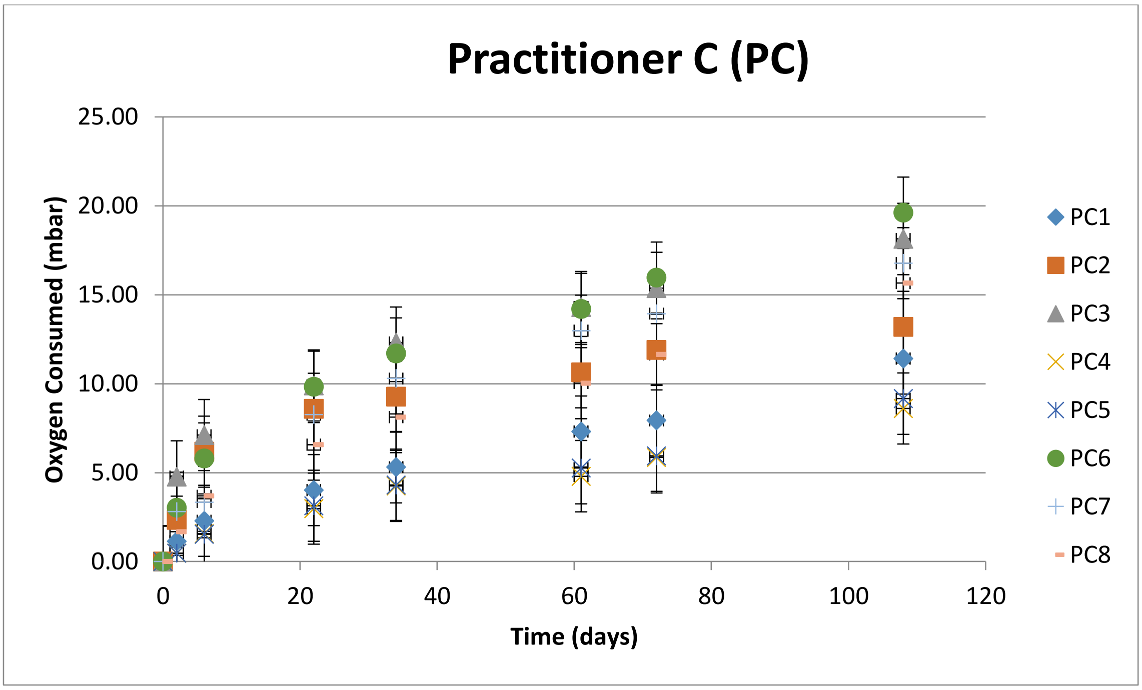


Figure 5.24 *Oxygen consumption of samples flame cleaned by Practitioner C and subsequently exposed to 90% RH.*

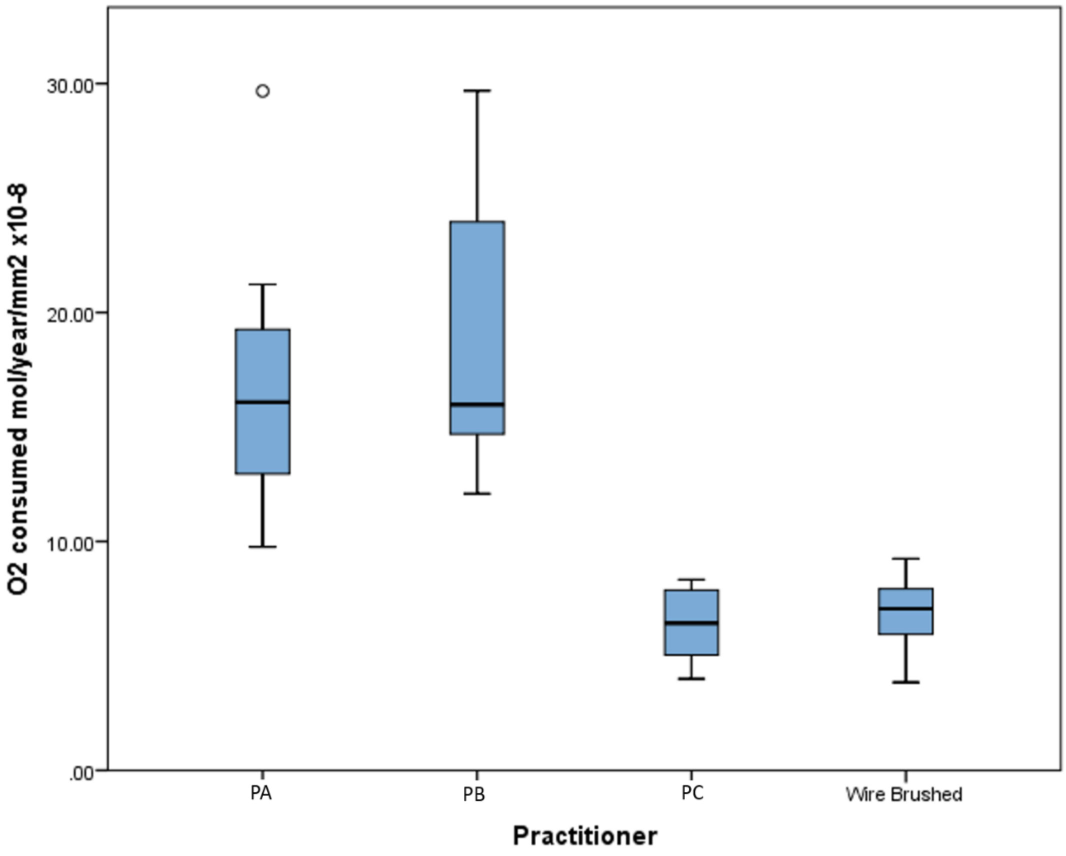


Figure 5.25 *Boxplot showing oxygen consumption (mol/year/mm2 x 10^{-8}) of samples flame cleaned by three heritage practitioners (PA, PB and PC) and the wire brushed gasometer substrate. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

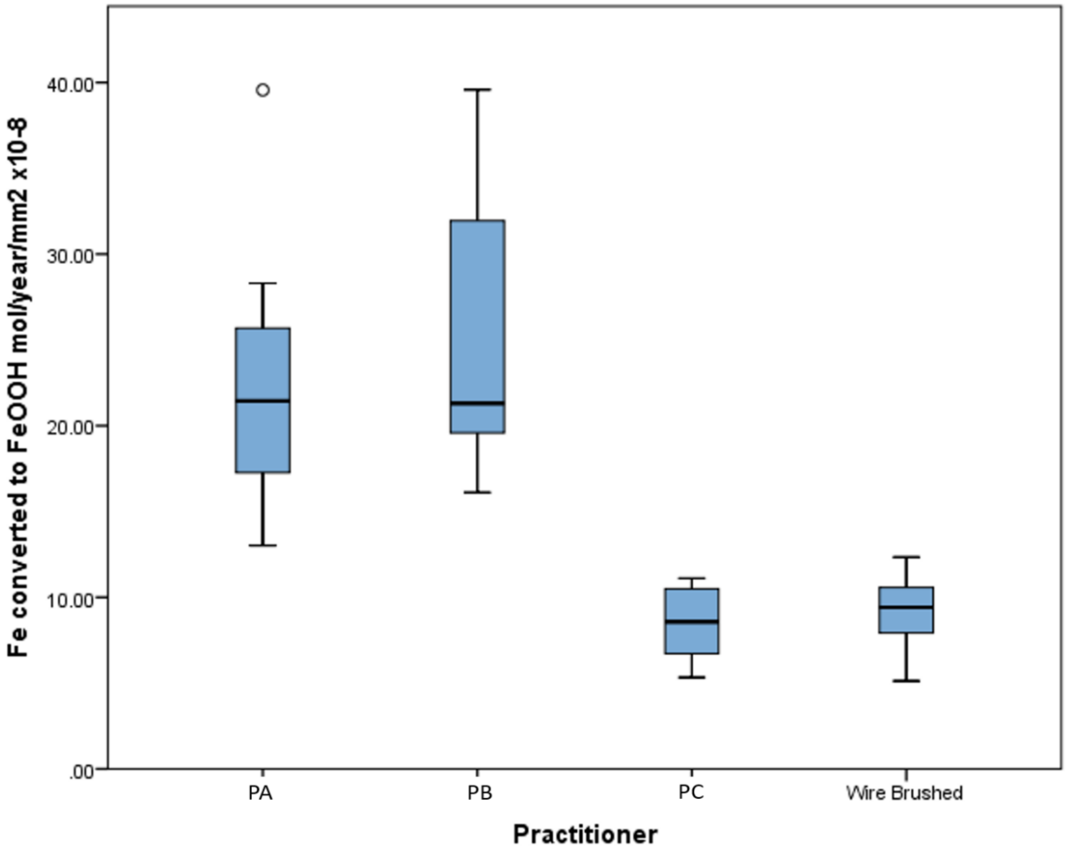


Figure 5.26 *Boxplot showing theoretical metallic iron converted to FeOOH (mol/year/mm2 x 10^{-8}) of samples flame cleaned by three heritage practitioners (PA, PB and PC) and wire brushed gasometer substrate. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

5.1.7 Scanning Electron Microscopy

Backscatter SEM images of uncleaned and laboratory flame cleaned gasometer sample material show a distinct fragmentation and de-adhesion of oxide layers opening channels to the metal surface (Figs 5.27-5.28).

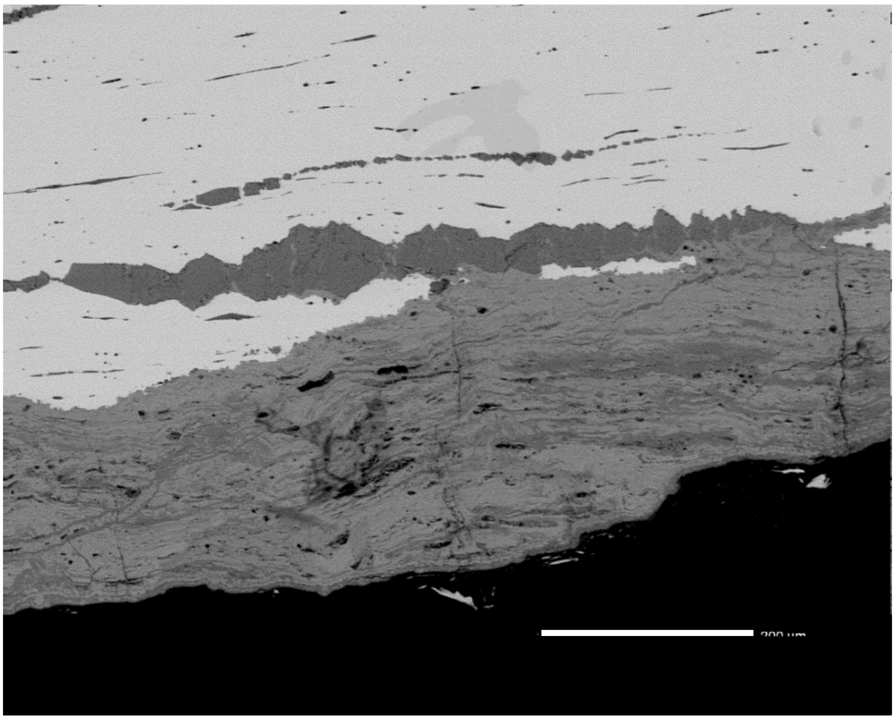


Figure 5.27 *Backscatter SEM image (x150 magnification) of a polished cross section of gasometer wrought iron showing characteristic slag inclusions and corrosion product layers. Scale bar 200µm.*

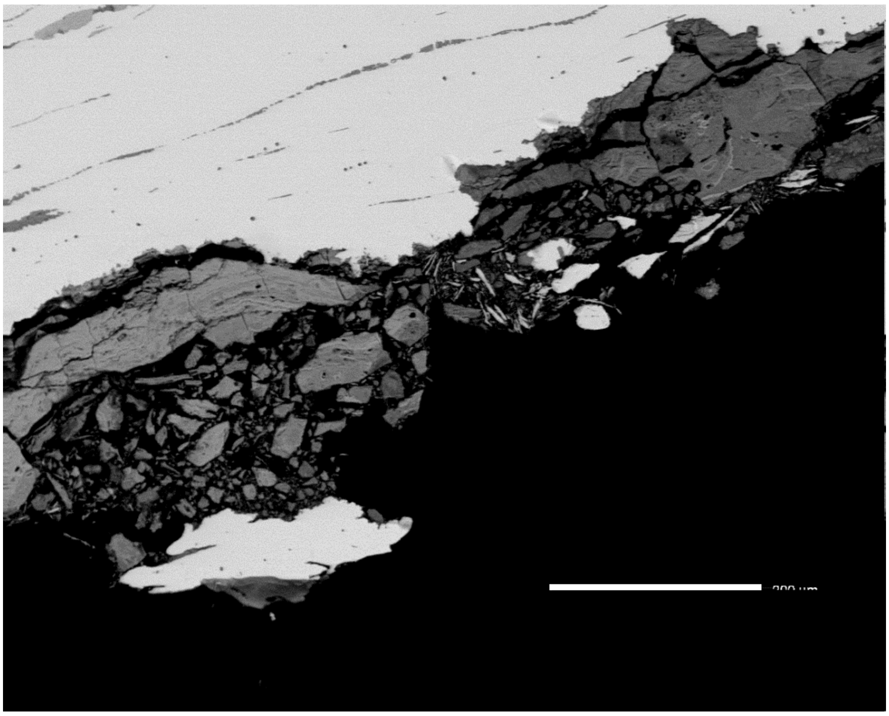


Figure 5.28 *Backscatter SEM image (x150 magnification) of a polished cross section of gasometer wrought iron after flame cleaning showing fragmentation of corrosion product layers. Scale bar 200µm.*

5.2 Investigating protective coatings for historic wrought iron

5.2.1 Gasometer sample characterisation

Slag inclusions are visible in transverse and longitudinal section (Fig. 5.29) showing rolling and piling of the wrought iron during its production. Inclusions are between 10-200µm and distributed in stringers in the direction of rolling. Fewer and smaller slag inclusions are present than in the railing sample material (Fig. 5.1) indicating a greater extent of working. Phosphorous is present (Table 5.5) although % composition is likely skewed by contamination by copper. Sulfur and chloride are indicated in the oxide layer consistent with atmospheric pollutants in the urban environment. Corrosion products identified by XRD (Fig. 5.31-5.33) of lepidocrocite, goethite and magnetite are also consistent with atmospheric corrosion.

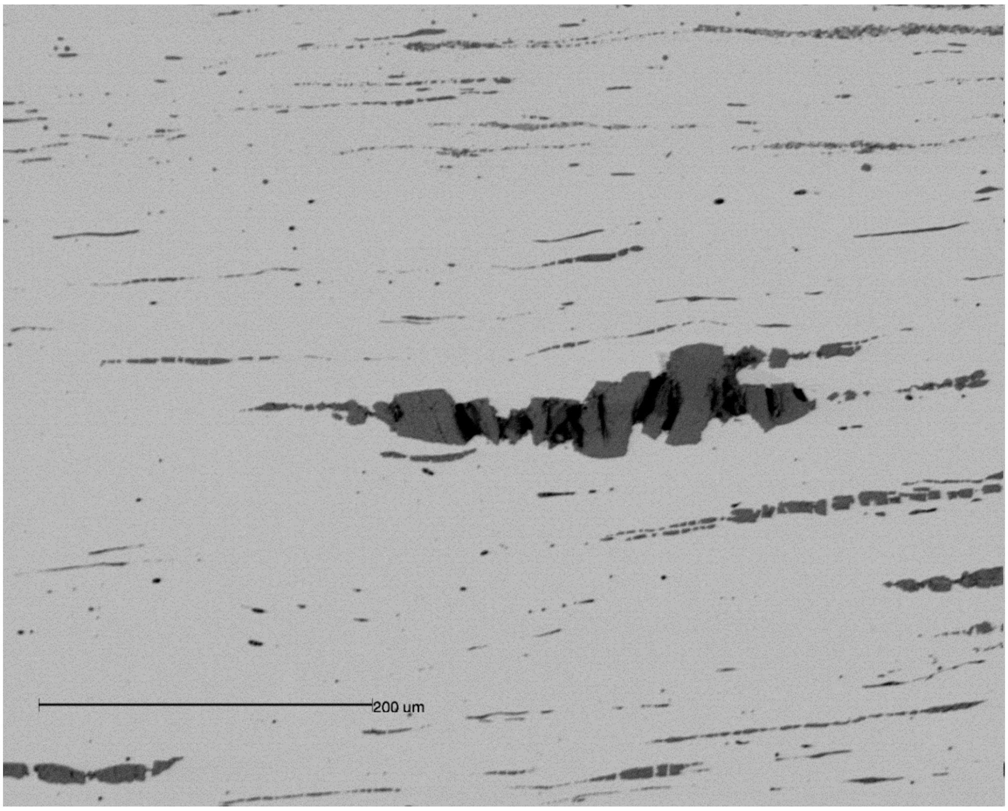


Figure 5.29 *Backscatter SEM image (x200 magnification) of a polished cross section of gasometer wrought iron showing characteristic slag inclusions.*

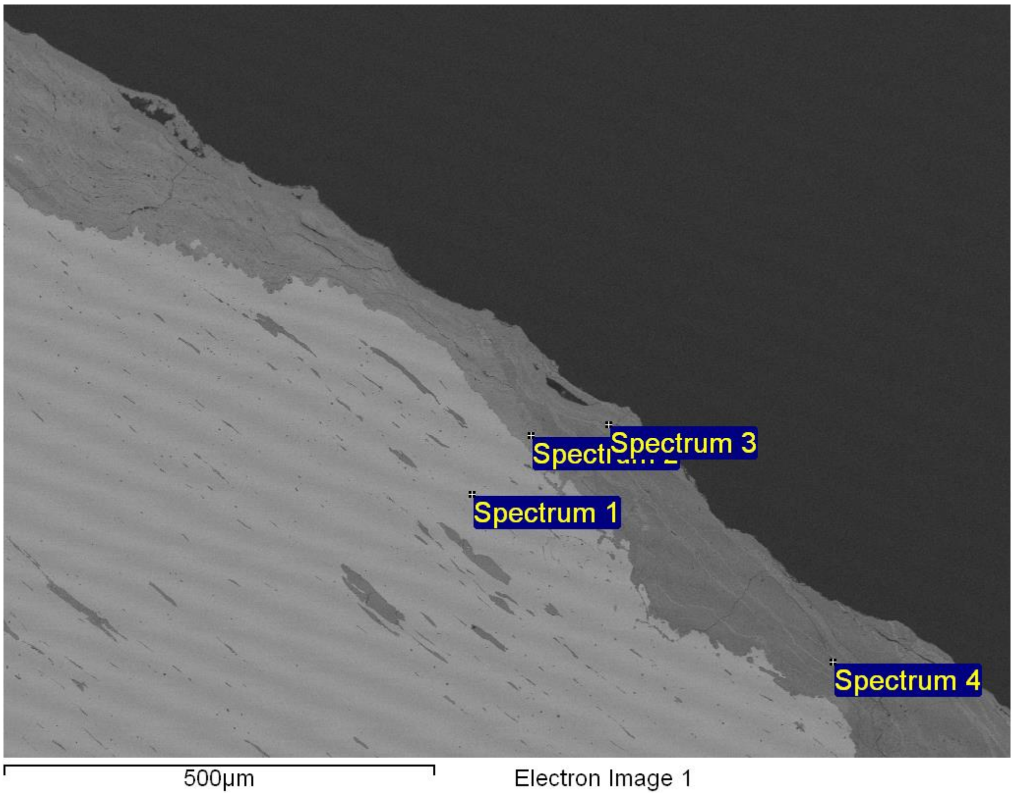
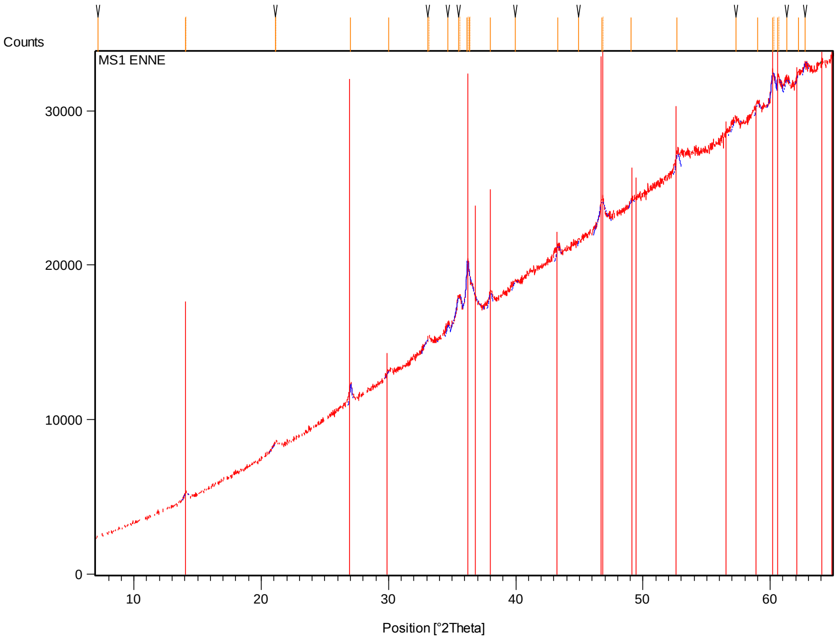


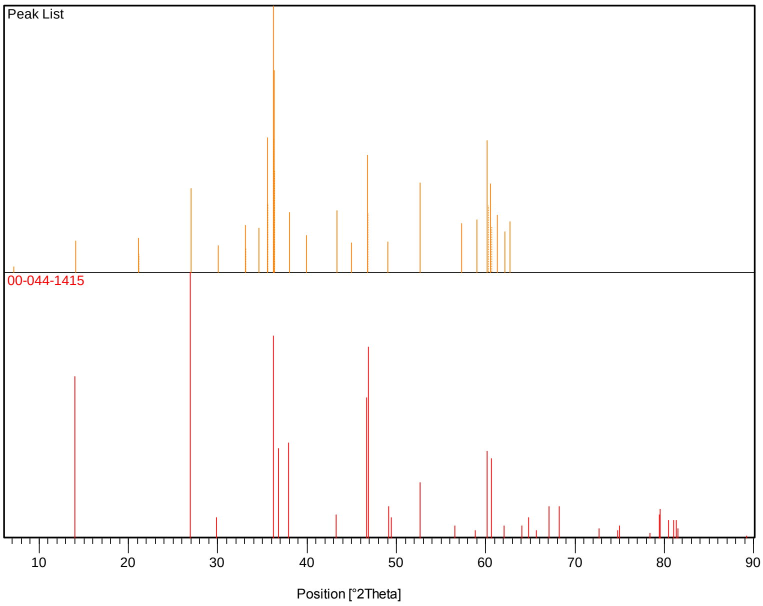
Figure 5.30 *Backscatter SEM image showing location of spectra for analysis of gasometer wrought iron.*

Spectrum	***O***	***P***	***S***	***Cl***	***Fe***	***Cu***	***Total***
Spectrum 1 Alloy		*0.55*			*99.15*	*0.3*	*100*
Spectrum 2 Oxides	*32.57*	*0.24*	*0.28*		*66.56*	*0.35*	*100*
Spectrum 3 Oxides	*30.88*				*68.7*	*0.42*	*100*
Spectrum 4 Oxides	*29.86*	*0.29*	*0.96*	*0.18*	*68.26*	*0.45*	*100*
Max.	*32.57*	*0.55*	*0.96*	*0.18*	*99.15*	*0.45*	
Min.	*29.86*	*0.24*	*0.28*	*0.18*	*66.56*	*0.3*	

Table 5.5 *Results of quantitative SEM analysis of gasometer wrought iron.*

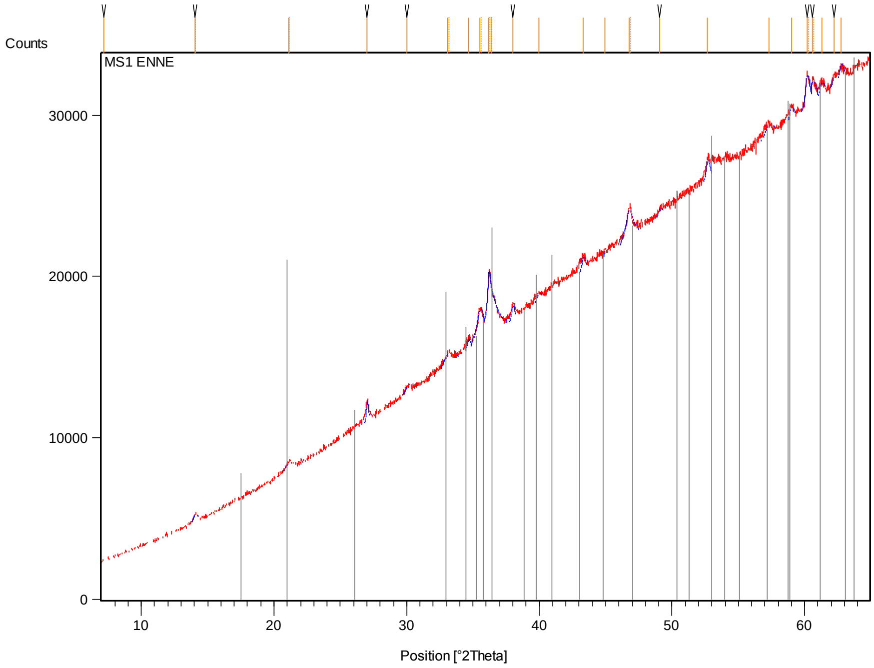


a)

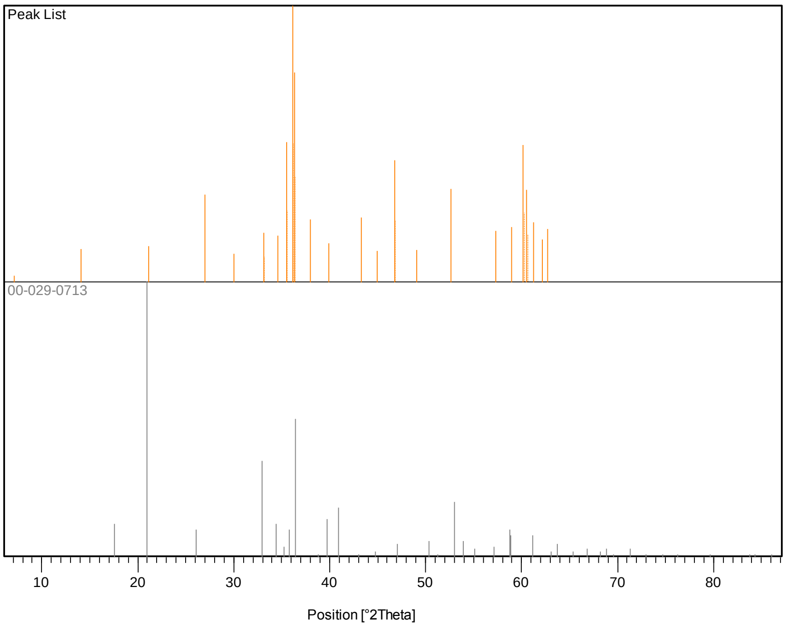


b)

Figure 5.31 a) *Diffractogram of corrosion products from gasometer sample material;* ***b)*** *patterns of identified corrosion product (uppermost pattern) indicating presence of lepidocrocite (00-044-1415 (lower pattern)).*

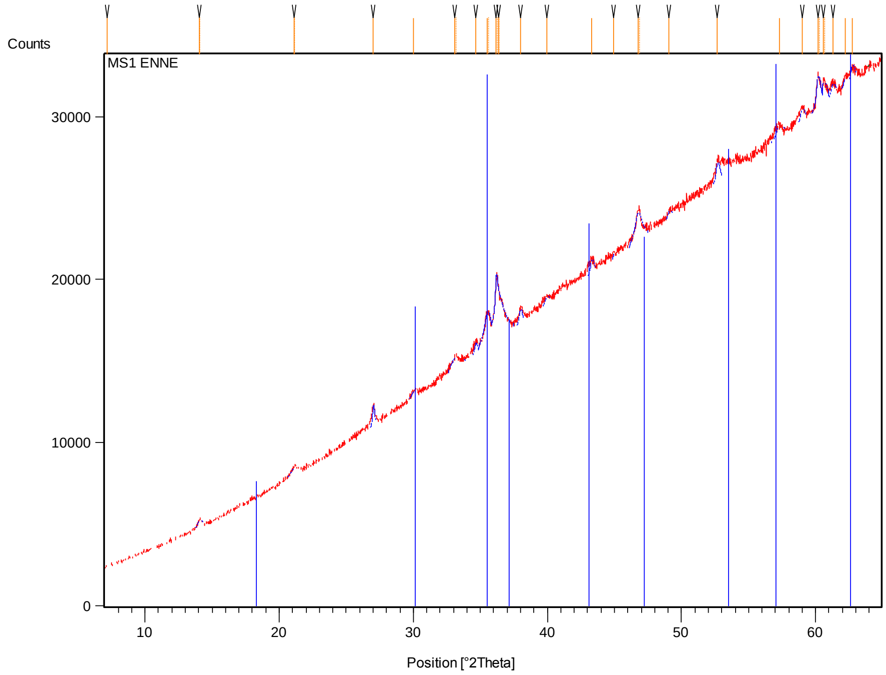


a)

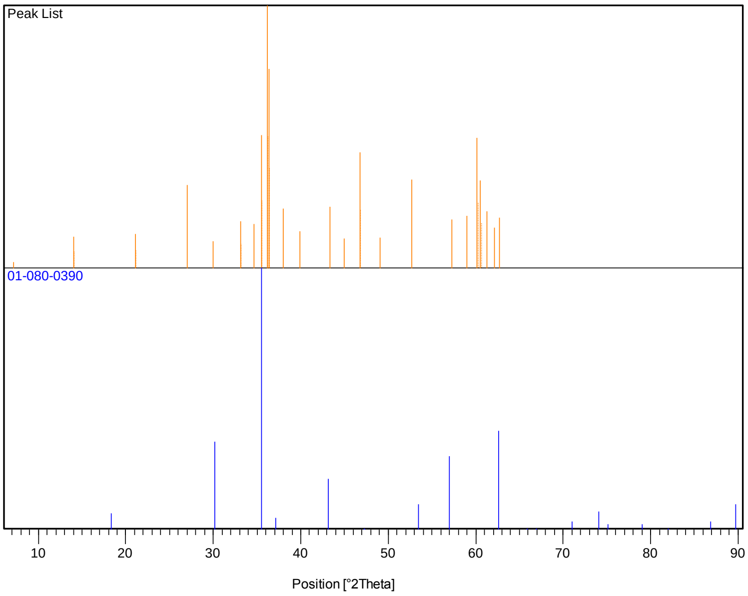


b)

Figure 5.32 a) *Diffractogram of corrosion products from gasometer sample material;* ***b)*** *patterns of identified corrosion product (uppermost pattern) indicating presence of goethite (00-029-0713 (lower pattern)).*



a)



b)

Figure 5.33 a) *Diffractogram of corrosion products from gasometer sample material;* ***b)*** *patterns of identified corrosion product (uppermost pattern) indicating presence of magnetite (01-080-0390 (lower pattern)).*

5.2.2 Prepared samples

Images of samples after surface preparation and addition of each coating are given (Fig. 5.34). Contrasting primer and build colours are evident allowing completeness of coverage to be ascertained. The high build of System A obscures the substrate surface morphology which is retained with Coating C. System B reduces visibility of morphology through settlement of slow curing topcoat into the pits and troughs of the surface. System A has a bulky, plastic appearance, System B a very high gloss and Coating C a matte finish and close conformation to the substrate surface.

Figure 5.34 *Prepared samples showing uncoated substrates and samples after application of each coating constituting the system. In the case of Coating C, there is only one coating applied.*

5.2.3 **Coating properties**

5.2.3.1 *Coating properties during application*

Coating properties during application influence success of the cured coating by dictating ease of application. The properties of System A (e.g. viscosity and completeness of curing) are dependent on correct mixing ratio of the two pack system. Its properties change over time during application as the curing reaction proceeds. Observations of application properties are given in Table 5.6. Curing of all coatings within System A was quicker than oil-based System B and Coating C coatings.

Coating		***Viscosity***	***Brush strokes/holidays***	***Curing***	***Comments***
System A	Primer	Initially low, becoming more viscous as reaction progresses	Significant pooling and run back from edges although less on the iron substrate than the glass.	Longer curing time than suggested by manufacturer	Need to make up in correct ratio of two parts – inconvenient and scope for mistakes. Longer curing – problem with two-pack ratio? Bubbles from stirring to mix – leave to stand. Difficult to clean brushes – time and expense of resources.
	Primer/ Build	Initially low, becoming more viscous as reaction progresses	Significant pooling and run back from edges- high gloss of cured primer exacerbates problem. Coverage and adhesion better on second application – reaction had progressed further and polymer was more viscous.	Slightly longer than primer but much quicker than the oil based coatings.	As above. Noticeable settling into pits in surface – leaves peaks with less depth of coating. Need to overcoat within 7 days.
	Topcoat	Initially low, becoming more viscous as reaction progresses	Very similar colour to Primer/Build – brush strokes difficult to discern. Not significant run back.	Longer than epoxy primer and build but much quicker than the oil based coatings.	As Primer.
System B	Primer	Low	Not pronounced on iron substrate, more so on glass despite blasting to provide key.	Rel. slow. Min. 6 hours between coats. 24 to overcoating.	Low viscosity means more, thinner coats which may minimise holidays and slumping.
	Topcoat	Low	Brush strokes visible immediately but low viscosity and slow curing allow levelling out for good coverage. Covers primer relatively well but some run back from corners and edges. Second coat adheres much more effectively despite high gloss – good adhesion possibly due to high tack.	Very slow. Still very tacky after a few days.	Bubbles created by stirring transfer to sample – leave to stand but not long enough to settle out.
Coating C		Very low	More brush strokes and run back on both substrates than experienced with System B. Partly an effect of the surface prep method for the iron substrate – wire brushing creates a polished surface with little keying. Second coat adheres more successfully.	Touch dry more quickly than System B.	Difficult to observe holidays with the second coat due to lack of contrast in appearance between coats.

Table 5.6 *Properties of coatings during application.*

5.2.3.2 *Properties of cured coatings*

Properties of the cured coatings influence and offer insight into their protective performance and aesthetic suitability for heritage contexts. They are summarised in Table 5.7 and illustrated in Figures 5.35-5.45. Holidays are access sites for ingress of water and aggressive species and are evident in System A build and topcoat, System B primer and Coating C. Brushstrokes indicate uneven build and of coatings and consequent uneven protection in barrier coatings where length of the diffusion pathway will be greater in peaks and shorter in troughs. These are evident in System A build and topcoat where they add to the plastic aesthetic and on System B primer where they are eventually obscured by settlement of slow-curing topcoat. Run back from edges is evident with Coating C and from edges and peaks with System B. These areas will be afforded less protection by the coatings.

The high build (Table 5.8) of System A (210 – 406µm) leads to a bulky appearance which obscures surface morphology of the wrought iron. Although System B build is lower (31 – 98µm) surface morphology is still obscured by the coating through settlement of coating into pits. Its appearance is characterised by the high gloss of the topcoat. Closely following the contours of the substrate, Coating C has the lowest build (DFT 11 – 64µm) as expected of the coating with fewest coats applied and a matte appearance.

Dry film thicknesses (DFT) show a wide range (Fig. 5.46) despite frequent recalibration of the meter to counter drift. This may be due to relative thicknesses of peaks and troughs of brushstrokes such as evident on System A samples (Fig. 5.37) which have the greatest range of thicknesses with outlying values. Different thicknesses of System B may be due to settlement of coating into pits and run back from peaks which have consequently lower thicknesses (Fig. 5.42). Coating C DFT measurements were calibrated on the uncoated substrate material with oxide layers which are measured by the meter as a coating. Variable thickness of the oxides may account for some of the range of Coating C DFT values.

Coating		Holidays visible (macroscopic)	Brushstrokes visible (macroscopic)	Runback from edges and peaks visible	Aesthetic of complete system
System A	**Primer**	Bubbles visible on all samples (3-10 per cm^2) particularly in pits (Fig. 5.35).	No	No	High gloss Plastic Bulky
	Build	No	Yes – more noticeable on less pitted reverse of samples (Fig. 5.37).	No	
	Topcoat	Pinholes from burst bubbles (1-2 per sample 12cm^2).	Yes (Fig. 5.38)	No	
System B	**Primer**	Pinholes visible on most samples (1-10 per cm^2) (Fig 5.39).	Yes (Fig. 5.40)	No	High gloss Surface morphology of metal visible
	Build	No pinholes. Peaks and runback create holidays on most samples.	No	All samples show run back from edges and peaks revealing primer (Fig. 5.42).	
Coating C		Yes – mostly visible in more pitted areas and where a greater thickness of coating has been applied (Fig. 5.43).	No	Noticeable thinner coating at edges and corners (Figs 5.44, 5.45).	Matte Surface morphology of metal visible

Table 5.7 *Properties of cured coatings.*

***Figure 5.35** Sample HSII08 showing bubbles in System A primer after curing (scale of background squares 10 x 10mm).*

***Figure 5.36** Sample HSII04 showing pinhole holidays in cured System A build coating* (scale of background squares 10 x 10mm).

Figure 5.37 *Sample HSII01 showing brushstrokes in cured System A build coating (scale of background squares 10 x 10mm).*

Figure 5.38 *Sample HSII08 showing pinholes in cured System A topcoat (scale of background squares 10 x 10mm).*

Figure 5.39 *Sample HSII16 showing pinhole holidays in cured System B primer (scale of background squares 10 x 10mm).*

Figure 5.40 *Sample HSII13 showing brushstrokes in cured System B primer (scale of background square 10 x 10mm).*

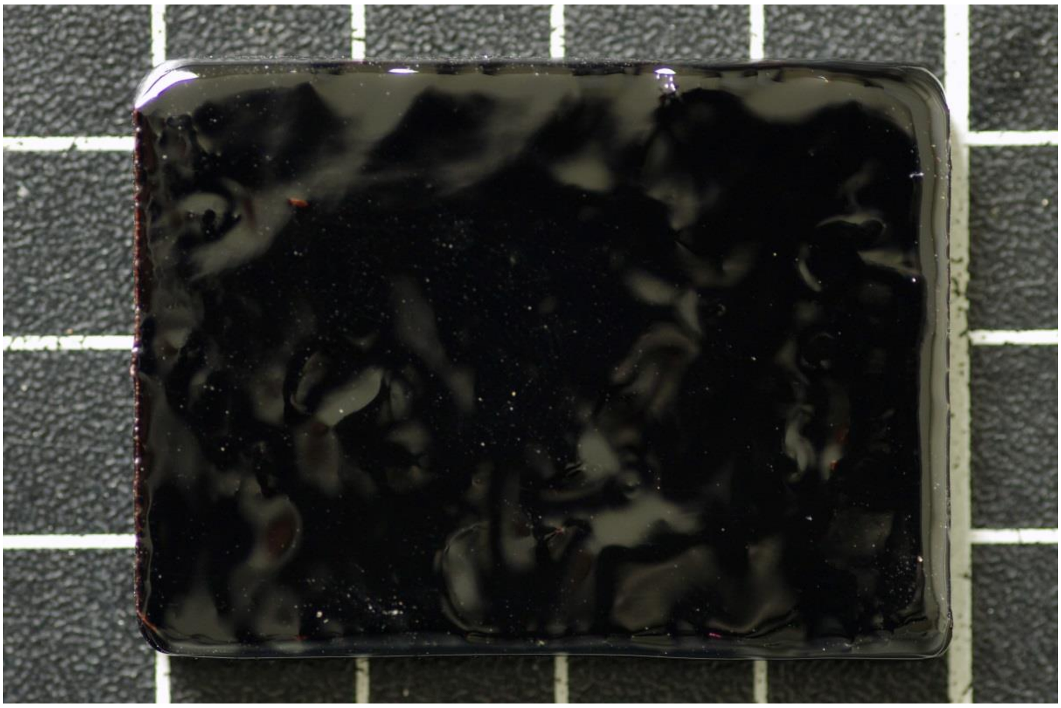


Figure 5.41 *Sample HSII18 showing peaks run back of System B topcoat from peaks revealing red primer (scale of background squares 10 x 10mm).*

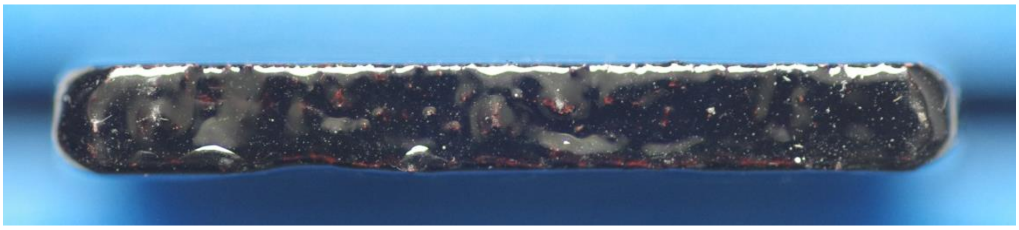


Figure 5.42 *Sample HSII11 showing run back of System B topcoat from peaks and edges (sample area shown 30mmx4mm).*

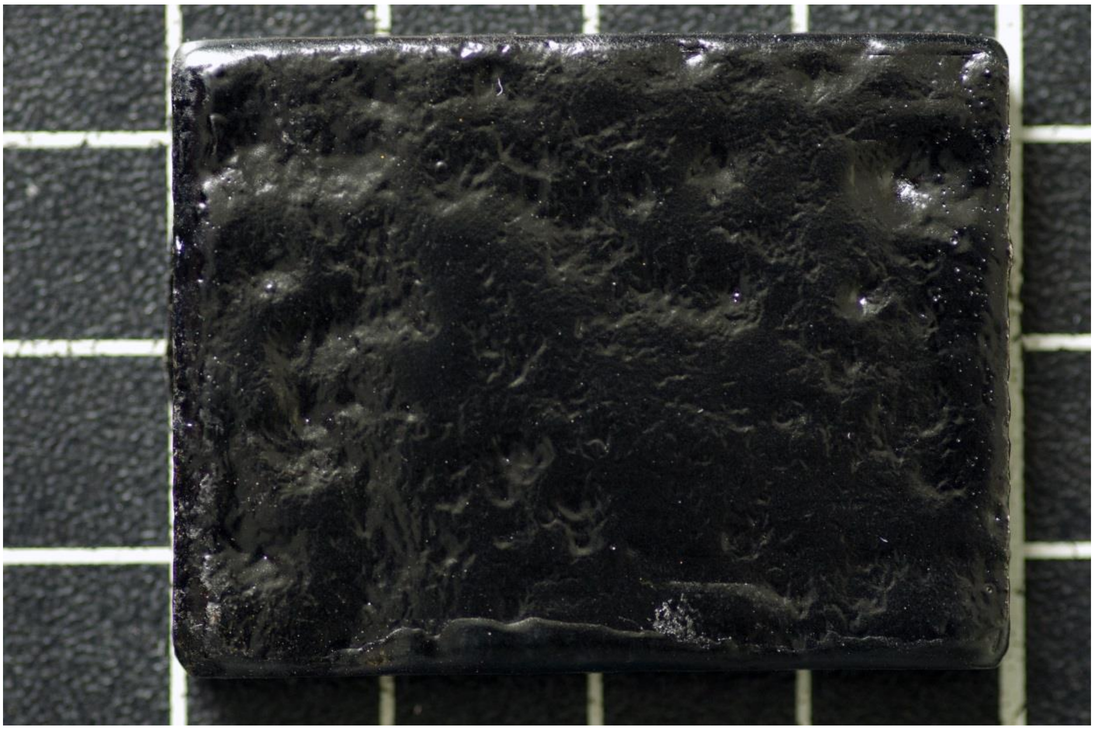


Figure 5.43 *Sample HSII26 showing pinholes in Coating C after curing (scale of background squares 10 x 10mm).*

Figure 5.44 *Sample HSII28 showing run back of cured Coating C from edges (sample area shown 40mmx4mm).*

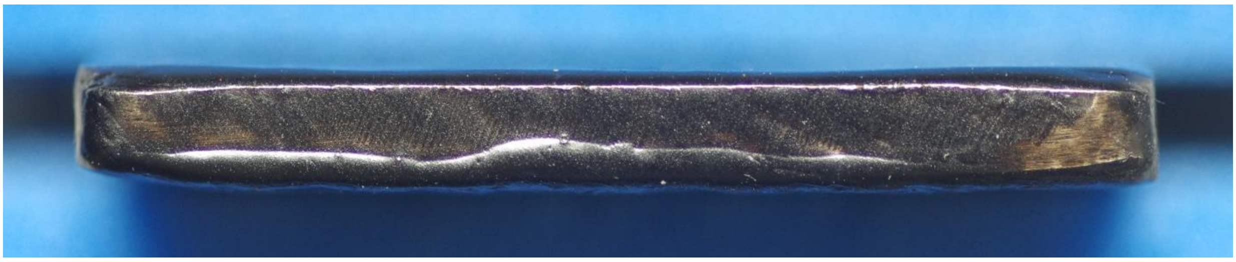


Figure 5.45 *Sample HSII22 showing areas missed during application of Coating C to sample edge (sample area shown 40mmx4mm).*

5.2.3.3 *Dry film thicknesses (DFT)*

	Coating		
	System A	*System B*	*Coating C*
Coating DFT (micron)	338	72	36
	332	31	62
	406	98	34
	280	23	33
	392	66	22
	322	80	38
	210	52	48
	316	64	45
	346	46	62
	340	88	64
	300	44	11
	318	36	58
Nominal (average) DFT (micron)	325	58	43

Table 5.8 *Dry film thicknesses of cured coatings.*

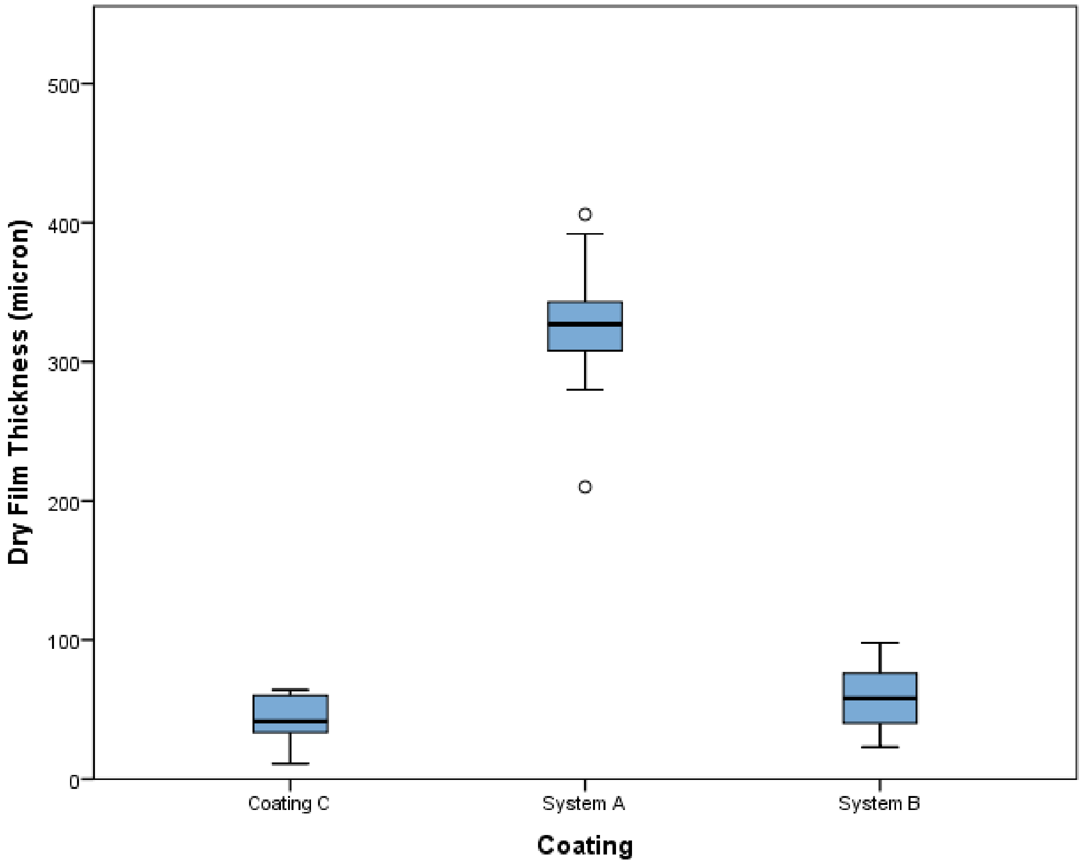


Figure 5.46 *Boxplot showing the dry film thicknesses of the cured coatings. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

5.2.3.4 *Pull-off adhesion testing*

Adhesion pull-off values are given in Table 5.9 and Figure 5.47 and modes of failure in Table 5.9 and illustrated in Figure 5.48. For each coating system the mode of failure was consistent between the test dollies. Coating C values are significantly lower than Systems A and B and its mode of failure is cohesive within the corrosion product layer rather than a failure of the coating. The value for adhesion of Coating C to the oxide layer must exceed these values. System A adhesion values are slightly higher than System B on the whole although there is an overlap in values. System A failure is consistently cohesive within the primer layer. System B failure is adhesive between the primer and the topcoat. With neither system is the substrate exposed after pull-off hence the adhesion value of the primers to the substrates must exceed these values. There is good agreement between the pull-off values between samples of each coating.

	Adhesion Pull-off Value (MPa)		
Dolly	*System A*	*System B*	*Coating C*
1	11.19	9.47	4.77
2	12.50	8.95	2.93
3	11.00	8.90	4.92
4	11.73	8.61	3.61
5	12.81	8.24	4.41
6	10.96	10.93	4.66
7	12.34	10.78	4.41
8	12.09	10.42	4.30
9	10.40	10.25	4.87
10	12.90	10.66	4.26
Mode of Failure	Cohesive within primer.	Adhesive between primer and topcoat.	Cohesive within corrosion product layer.

Table 5.9 *Adhesion pull-off values (MPa) and modes of failure.*

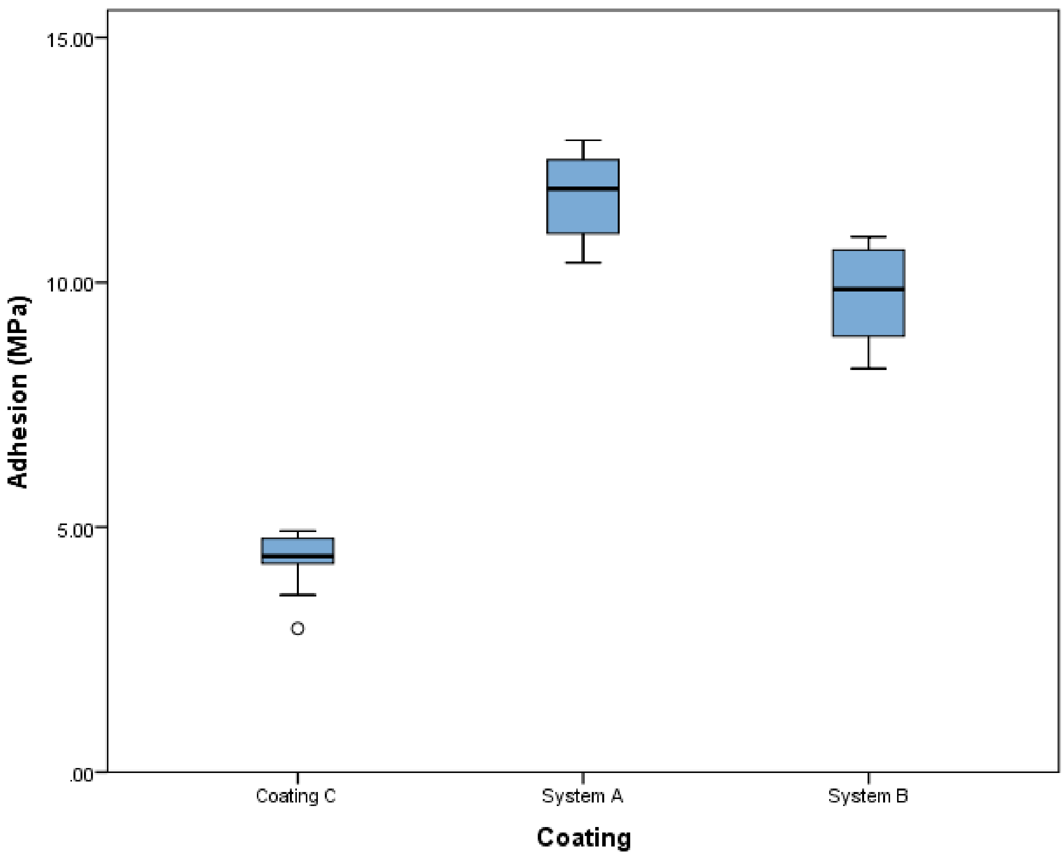


Figure 5.47 *Boxplot showing adhesion pull-off values for coatings. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

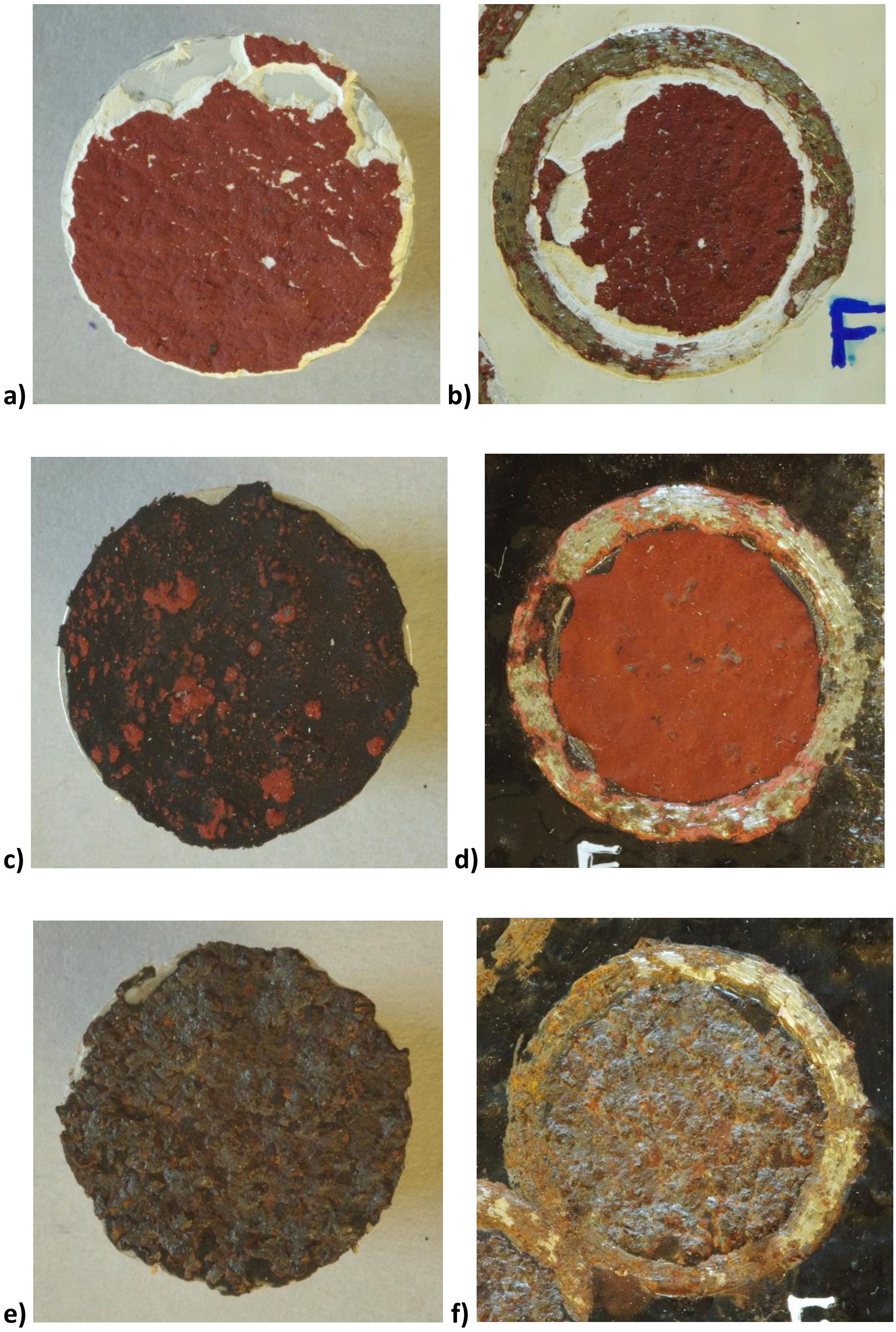


Figure 5.48 *Pull-off dollies (left) and corresponding areas of coated samples (right) showing modes of failure. Dollies and pull-off areas have a diameter of 20mm.* ***a), b)*** *System A with failure cohesive within the primer;* ***c), d)*** *System B with failure mostly adhesive between primer and topcoat;* ***e), f)*** *Coating C with failure cohesive within corrosion products.*

5.2.4 Oxygen consumption and corrosion rates of coated samples

All coated samples consumed oxygen during the test period. Raw consumption graphs for all coated metal samples are given in Figures 5.49-5.51 and for coated control samples (glass substrates) in Figures 5.52-5.54. Agreement between the samples is good indicating a level of standardisation of sample preparation and coating application. The majority of oxygen consumption of the coated metal samples is accounted for by the consumption of the coating controls.

Oxygen consumption rates fall off after an initial high consumption rate for all samples. This is most pronounced with System A epoxy coating. Alkyd oil-based System B and Coating C exhibit greater oxygen consumption overall as expected in relation to their chemistry and oxidative cross-linking. Oxygen consumption by the coatings may be a predominantly surface phenomenon or a bulk process from within the coating. Below a critical pigment volume concentration, curing of alkyd coatings proceeds along a microscopic reaction front limited by diffusion of oxygen; above this concentration, reaction appears to be homogeneous (Erich et al. 2008). As the pigment volume concentration of these coatings is not available from the manufacturer, both manners of curing must be considered. Average oxygen consumption of the controls for each coating system have been subtracted from the coated wrought iron sample consumptions according to surface area of the coatings (Table 5.10, Figs 5.55 & 5.56) and by mass of coatings applied (Table 5.11, Figs 5.57 & 5.58) for comparison.

By both calculation methods, Coating C samples consumed no oxygen beyond the error of the oxygen meter. System A sample results were most affected by the method of calculating coating consumption due to their greater mass of coating. By both calculation methods, oxygen consumption was minimal but more so when calculated by mass of coating. System B sample results show oxygen consumption beyond that of the coating indicating corrosion of the underlying metal substrate.

When compared to the corrosion rate of the uncoated substrate sample material (Figs 5.56 & 5.57), whether calculated by mass or surface area, System A and Coating C significantly reduce corrosion rate of the wrought iron (Table 5.12). System B also reduces the corrosion rate but not to a statistically significant degree. In keeping with surface preparation testing results (5.13), uncoated samples with retained oxides exhibited a slower corrosion rate than aluminium oxide Sa2.5 blasted samples but blasting and applying System A also offers a reduced corrosion rate relative to uncoated substrate with retained oxides.

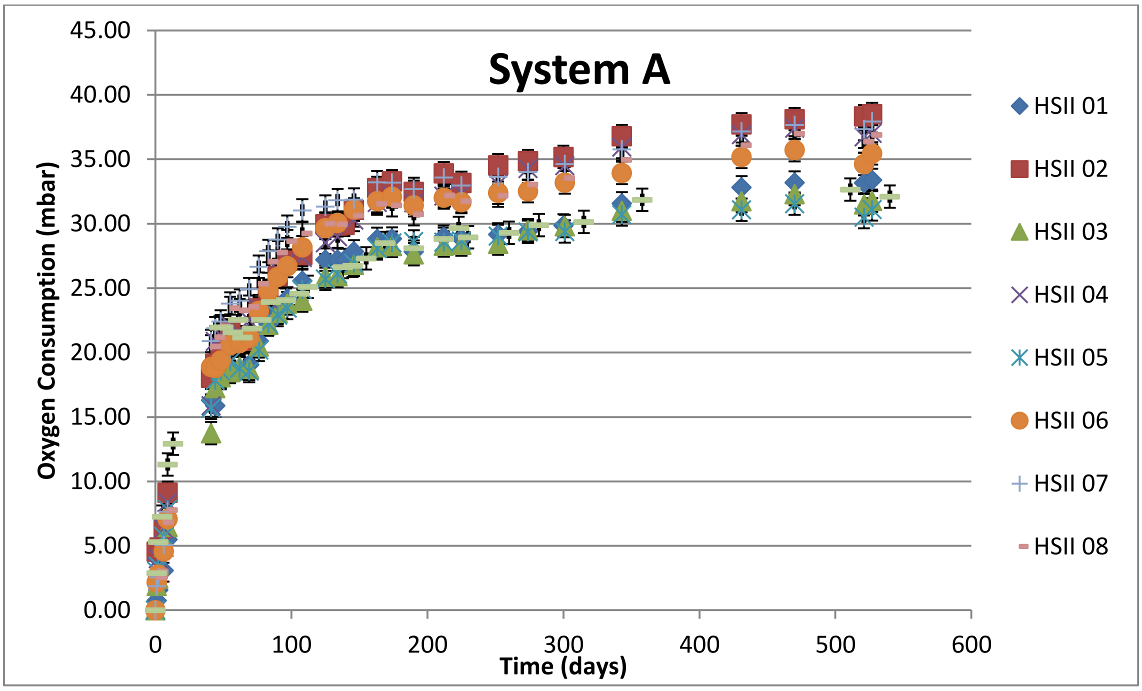


***Figure 5.49** Oxygen consumption of wrought iron samples coated with coating System A and subsequently exposed to 90% RH.*

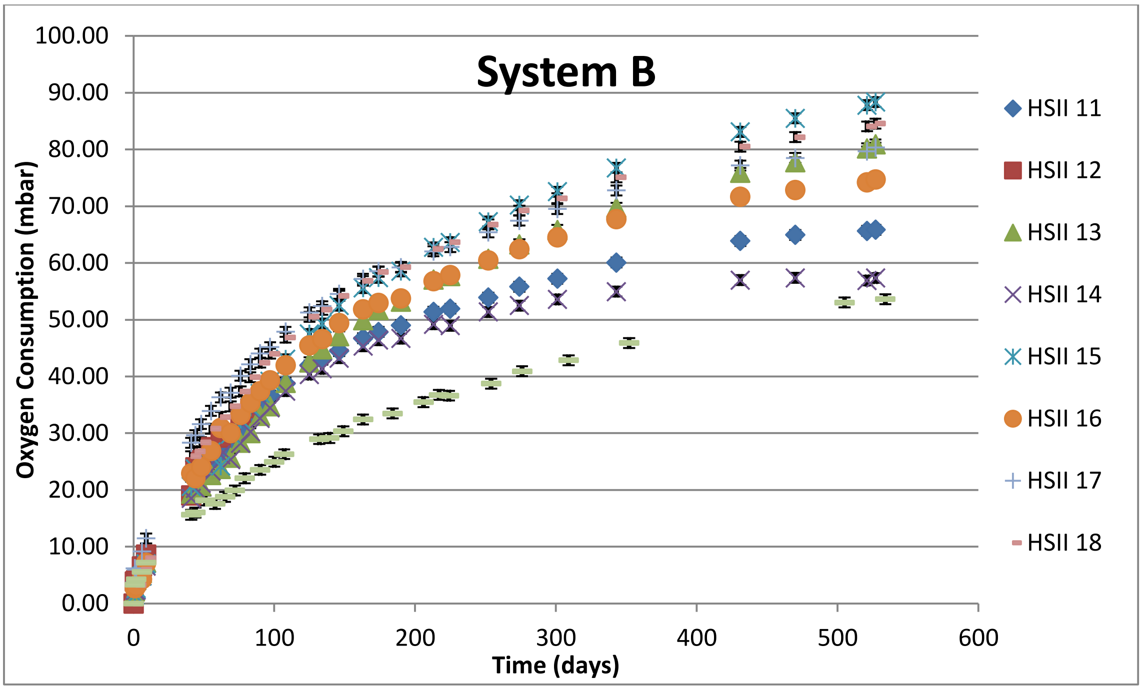


Figure 5.50 *Oxygen consumption of wrought iron samples coated with coating System B and subsequently exposed to 90% RH.*

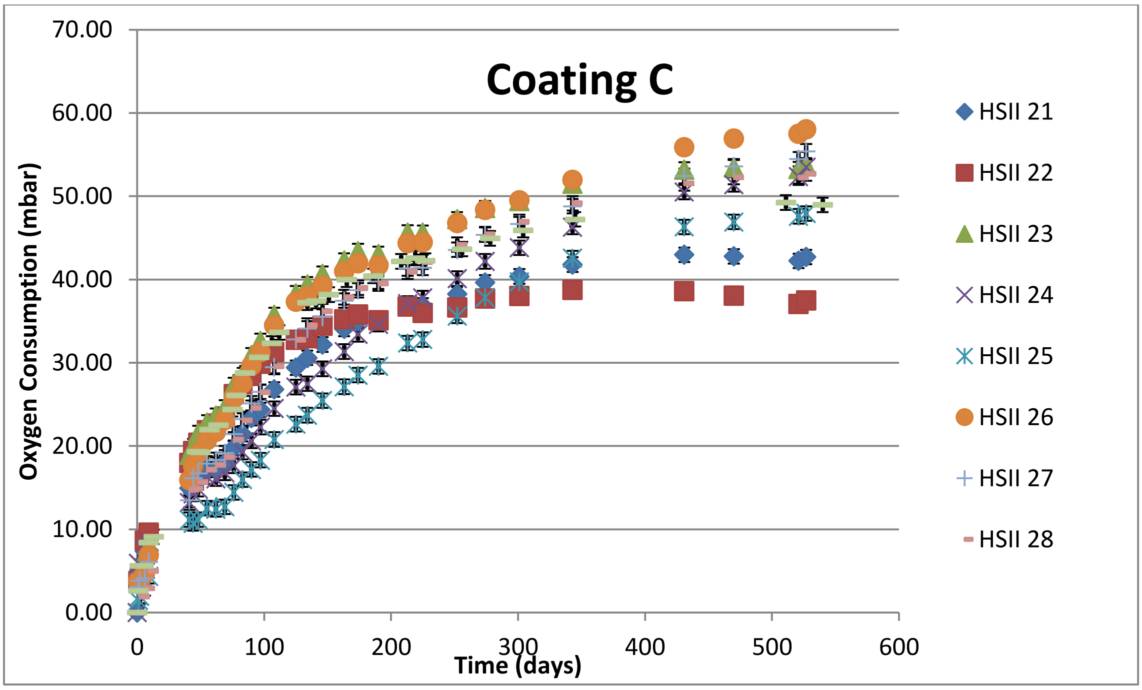


Figure 5.51 *Oxygen consumption of wrought iron samples coated with Coating C and subsequently exposed to 90% RH.*

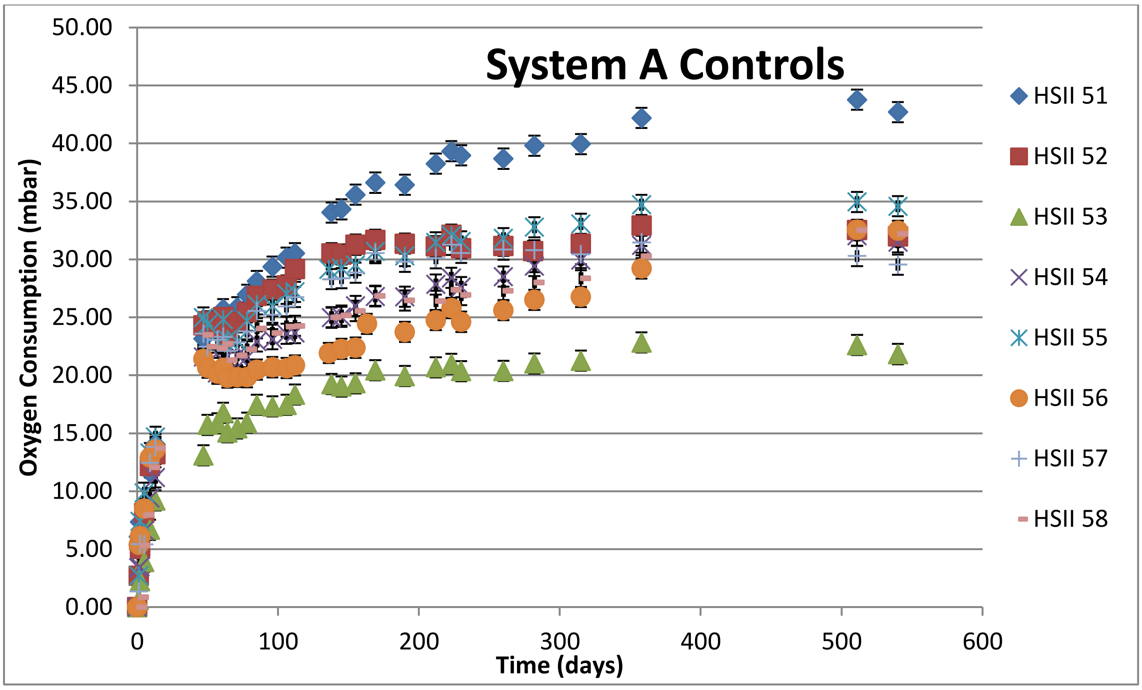


Figure 5.52 *Oxygen consumption of glass control samples coated with coating System A and subsequently exposed to 90% RH.*

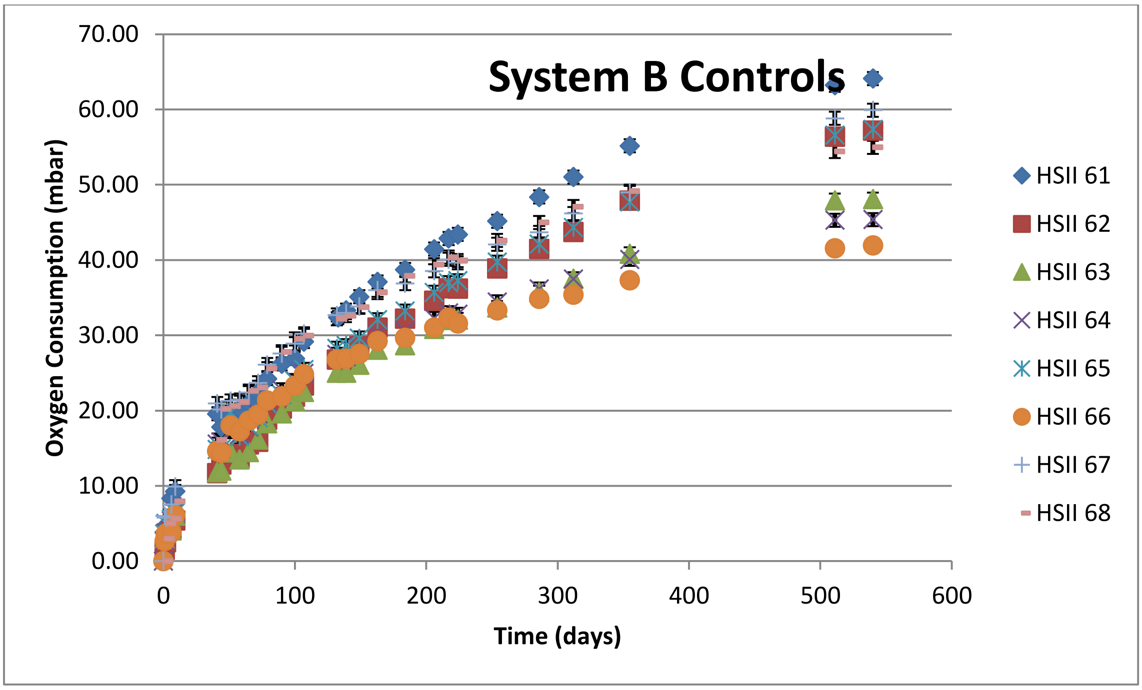


Figure 5.53 *Oxygen consumption of glass control samples coated with coating System B and subsequently exposed to 90% RH.*

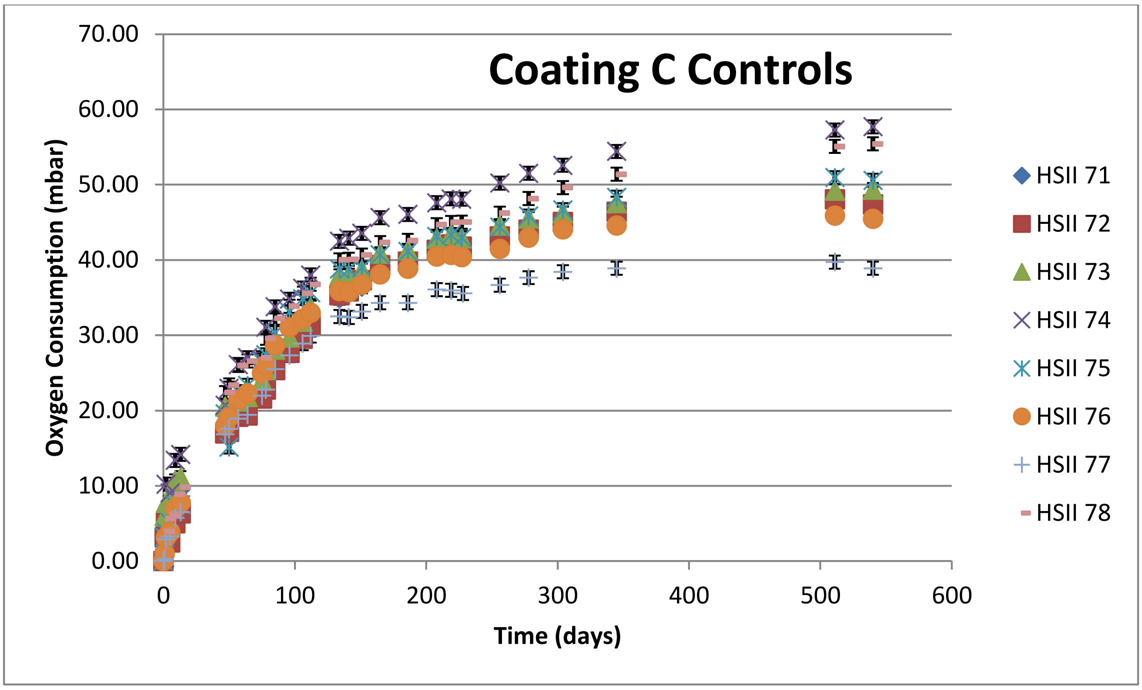


Figure 5.54 *Oxygen consumption of glass control samples coated with Coating C and subsequently exposed to 90% RH.*

Coatings	Sample	O$_2$ Consumption (mol/year/mm^2 x10^{-8})	Average O$_2$ Consumption (mol/year/mm^{2}x10^{-8})	Fe Converted to FeOOH (mol/year/mm^2 x10^{-8})	Average Fe Converted to FeOOH (mol/year/mm^2 x10^{-8})
System A	HSII01	0.40	0.45	0.53	0.60
	HSII02	1.42		1.90	
	HSII03	0.35		0.47	
	HSII04	0.32		0.43	
	HSII05	-0.26		-0.35	
	HSII06	0.62		0.83	
	HSII07	0.41		0.55	
	HSII08	0.06		0.08	
System B	HSII11	1.50	1.53	2.00	2.05
	HSII12	0.60		0.79	
	HSII13	1.90		2.53	
	HSII14	0.13		0.17	
	HSII15	2.70		3.60	
	HSII16	0.94		1.26	
	HSII17	2.43		3.24	
	HSII18	2.07		2.77	
Coating C	HSII21	-1.94	N/A	-2.59	N/A
	HSII22	-1.30		-1.73	
	HSII23	-0.02		-0.03	
	HSII24	-0.12		-0.16	
	HSII25	-2.64		-3.52	
	HSII26	-0.79		-1.05	
	HSII27	-1.25		-1.67	
	HSII28	-1.69		-2.26	
Wire Brushed Control (uncoated)	HSII31	5.44	5.52	7.25	7.36
	HSII32	5.47		7.30	
	HSII33	5.07		6.76	
	HSII34	5.29		7.06	
	HSII35	5.72		7.63	
	HSII36	5.40		7.20	
	HSII37	7.14		9.52	
	HSII38	4.59		6.12	
Sa2.5 Control (uncoated)	HSII41	7.30	6.87	9.73	9.16
	HSII42	6.86		9.15	
	HSII43	5.52		7.36	
	HSII44	3.84		5.12	
	HSII45	7.26		9.68	
	HSII46	8.56		11.41	
	HSII47	6.36		8.48	
	HSII48	9.25		12.34	

***Table 5.10** Results of oxygen consumption testing of coated wrought iron samples giving moles of oxygen consumed and theoretical moles of Fe converted to FeOOH per year per mm^2 x10^{-8}. Values have been calculated by subtracting oxygen consumption of the control samples of the coatings according to surface area of the coating applied to the wrought iron samples.*

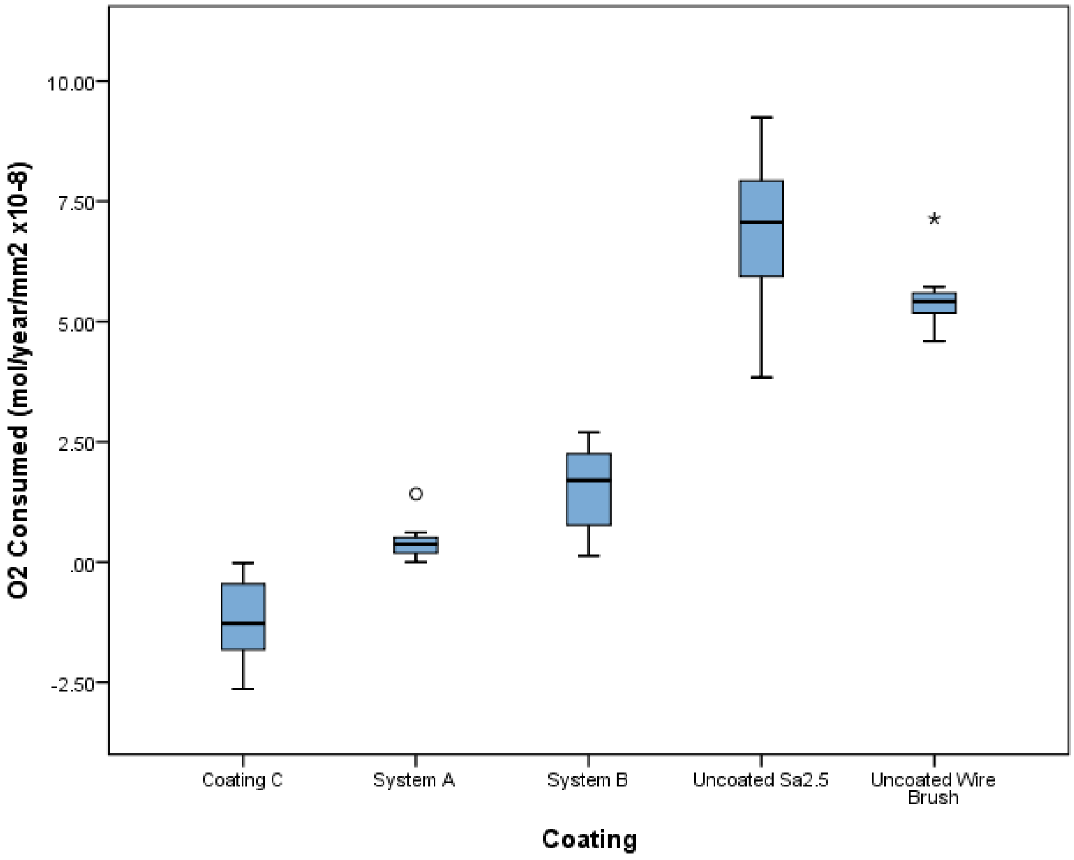


Figure 5.55 *Boxplot showing oxygen consumed by coated and uncoated samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. Oxygen consumption of the coatings has been calculated using the surface area of coating applied. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

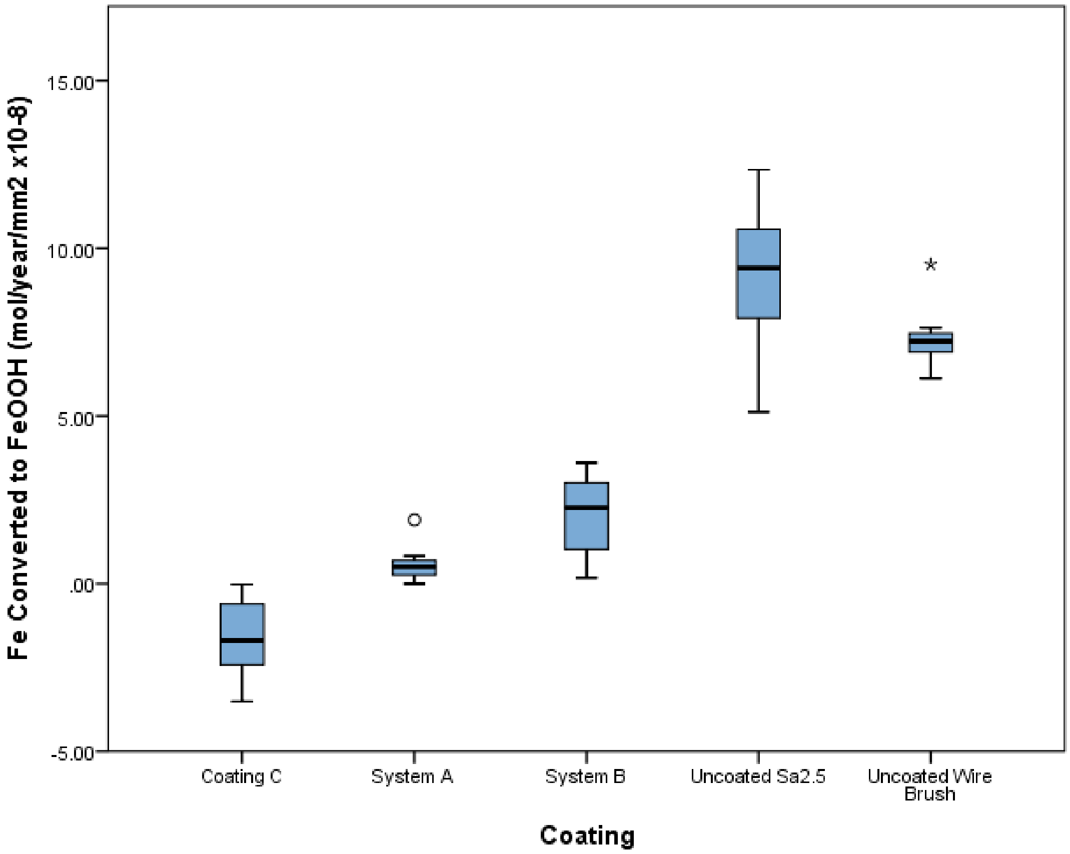


Figure 5.56 *Boxplot showing theoretical metallic iron converted to FeOOH by coated and uncoated samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. Oxygen consumption of the coatings has been calculated using the surface area of coating applied. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

Coating	Sample	O_2 Consumption (mol/year/ mm^2x10^{-8})	Average O_2 Consumption (mol/year/ mm^2x10^{-8})	Fe Converted to FeOOH (mol/year/mm^2 x10^{-8})	Average Fe Converted to FeOOH (mol/year/ mm^2x10^{-8})
System A	HSII01	-0.33	0.05	-0.44	0.07
	HSII02	0.47		0.63	
	HSII03	-0.37		-0.49	
	HSII04	0.40		0.53	
	HSII05	-0.47		-0.63	
	HSII06	0.16		0.22	
	HSII07	0.46		0.62	
	HSII08	0.09		0.11	
System B	HSII11	0.53	1.42	0.71	1.89
	HSII12	0.36		0.48	
	HSII13	1.55		2.07	
	HSII14	-0.16		-0.22	
	HSII15	2.56		3.41	
	HSII16	1.30		1.73	
	HSII17	2.49		3.32	
	HSII18	2.72		3.63	
Coating C	HSII21	-0.92	N/A	-1.22	N/A
	HSII22	-1.52		-2.03	
	HSII23	0.55		0.73	
	HSII24	-0.27		-0.37	
	HSII25	-0.91		-1.22	
	HSII26	0.31		0.41	
	HSII27	0.01		0.01	
	HSII28	-0.33		-0.44	
Wire Brushed Control (uncoated)	HSII31	5.44	5.52	7.25	7.36
	HSII32	5.47		7.30	
	HSII33	5.07		6.76	
	HSII34	5.29		7.06	
	HSII35	5.72		7.63	
	HSII36	5.40		7.20	
	HSII37	7.14		9.52	
	HSII38	4.59		6.12	
Sa2.5 Control (uncoated)	HSII41	7.30	6.87	9.73	9.16
	HSII42	6.86		9.15	
	HSII43	5.52		7.36	
	HSII44	3.84		5.12	
	HSII45	7.26		9.68	
	HSII46	8.56		11.41	
	HSII47	6.36		8.48	
	HSII48	9.25		12.34	

Table 5.11 *Results of oxygen consumption testing of coated wrought iron samples giving moles of oxygen consumed and moles of metallic iron converted to FeOOH per year per* mm^2 *x*10^{-8}*. Values have been calculated by subtracting oxygen consumption of the control samples of the coatings according to the mass of coating applied to the wrought iron samples.*

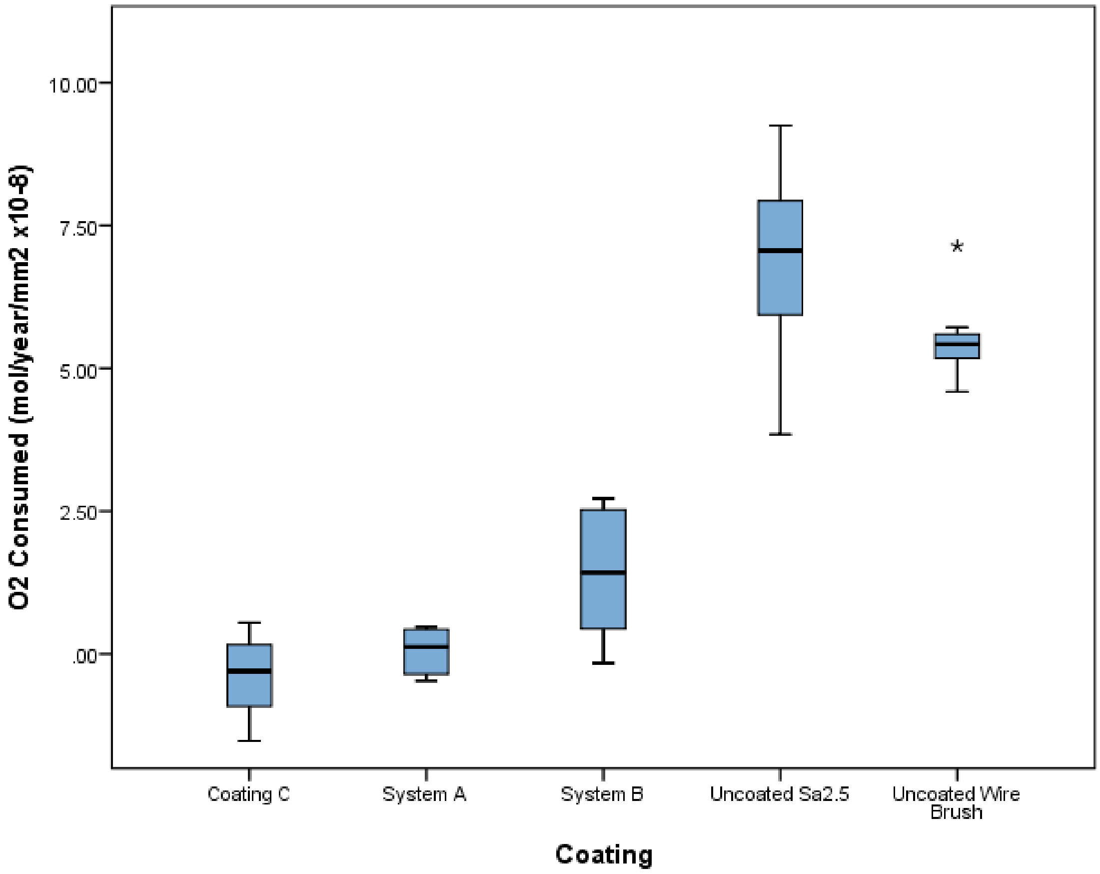


Figure 5.57 *Boxplot showing oxygen consumed by coated and uncoated samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. Oxygen consumption of the coating is calculated using the mass of coating applied. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

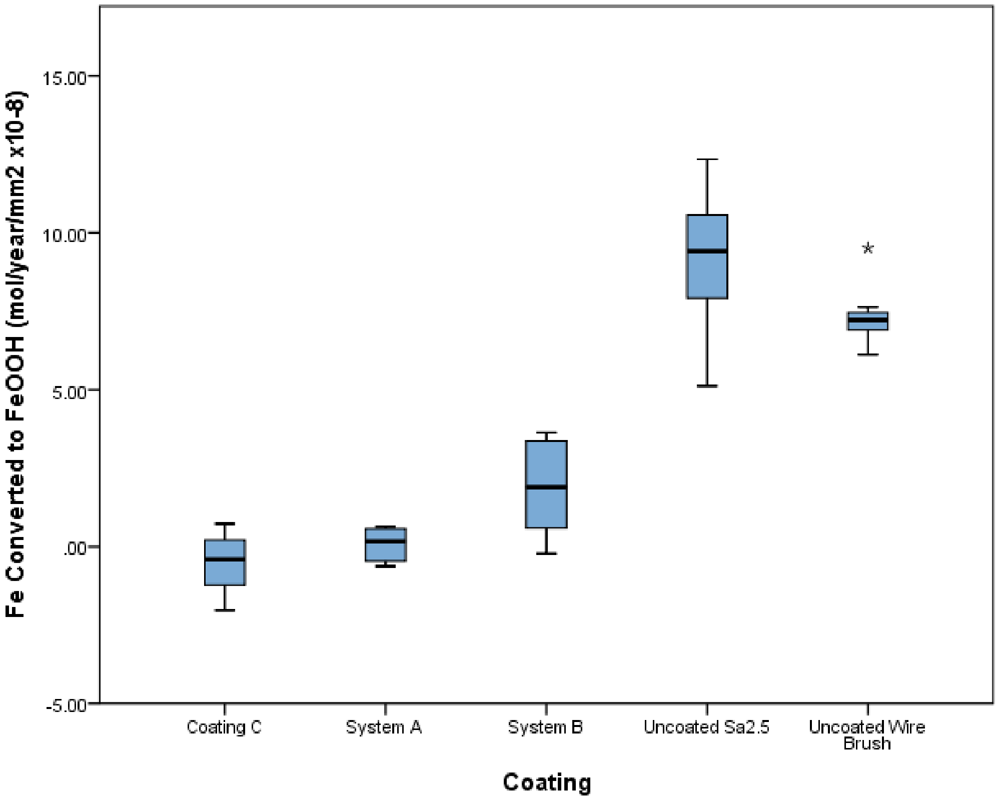


Figure 5.58 *Boxplot showing theoretical metallic iron converted to FeOOH by coated and uncoated samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. Oxygen consumption of the coatings is calculated using the mass of coating applied. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

Significantly different oxygen consumption and Fe converted to FeOOH (mol/year/mm^2)	
Coating oxygen consumption calculated by mass	*Coating oxygen consumption calculated by surface area*
Coating C / Uncoated Wire Brushed System A / Uncoated Sa2.5	Coating C / Uncoated Wire Brushed System A / Uncoated Sa2.5 System A / Uncoated Wire Brushed

Table 5.12 *Significantly different oxygen consumption and theoretical metallic iron conversion to FeOOH (mol/year/per mm^2 of iron) between coated samples and uncoated substrates (calculated by Kruskal-Wallis and with a significance level of 0.05).*

Following 90% RH exposure testing, System A samples showed damage to the polyurethane topcoat caused by small movements of the samples within the reaction vessels (Figs 5.59, 5.60). Notable on System B samples was particulate pick-up (Fig. 5.61) but no other damage. Coating C samples appeared unchanged even where the coating had a low build at edges (Fig. 5.63).

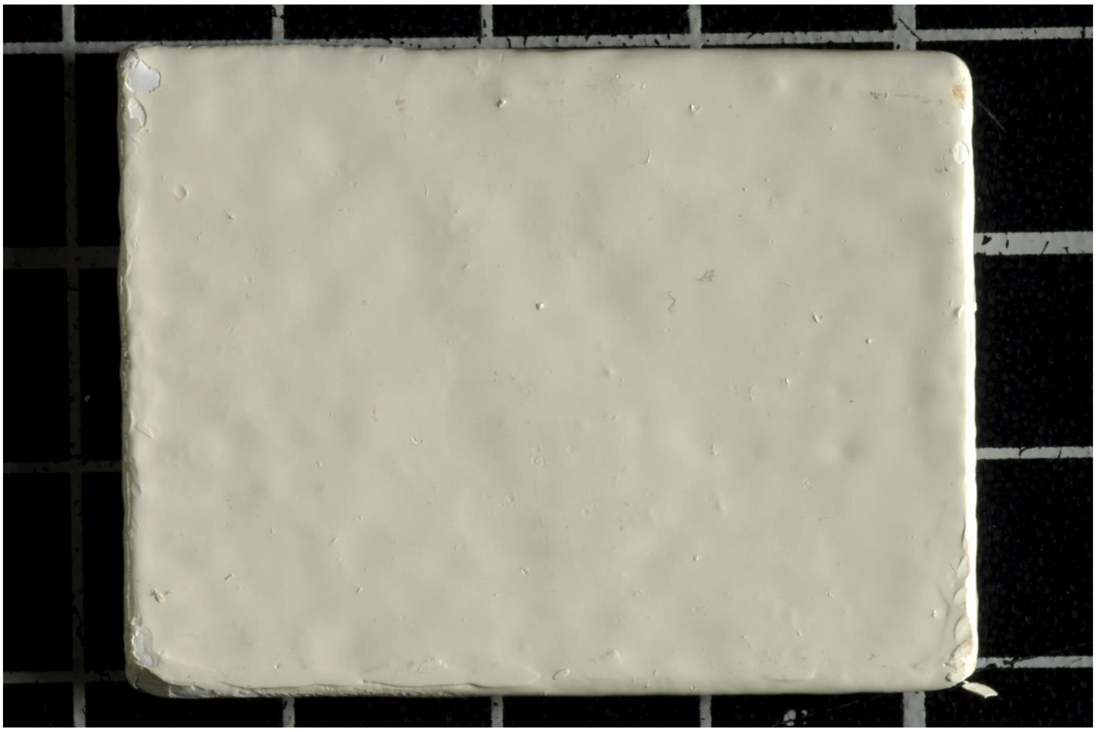


Figure 5.59 *Sample HSII02 after exposure to 90%RH for 540 days showing damage to corners but otherwise unchanged appearance.*

Figure 5.60 *Sample HSII02 showing damage to topcoat of System A after 90%RH exposure (scale of background scale 10mm between white lines).*

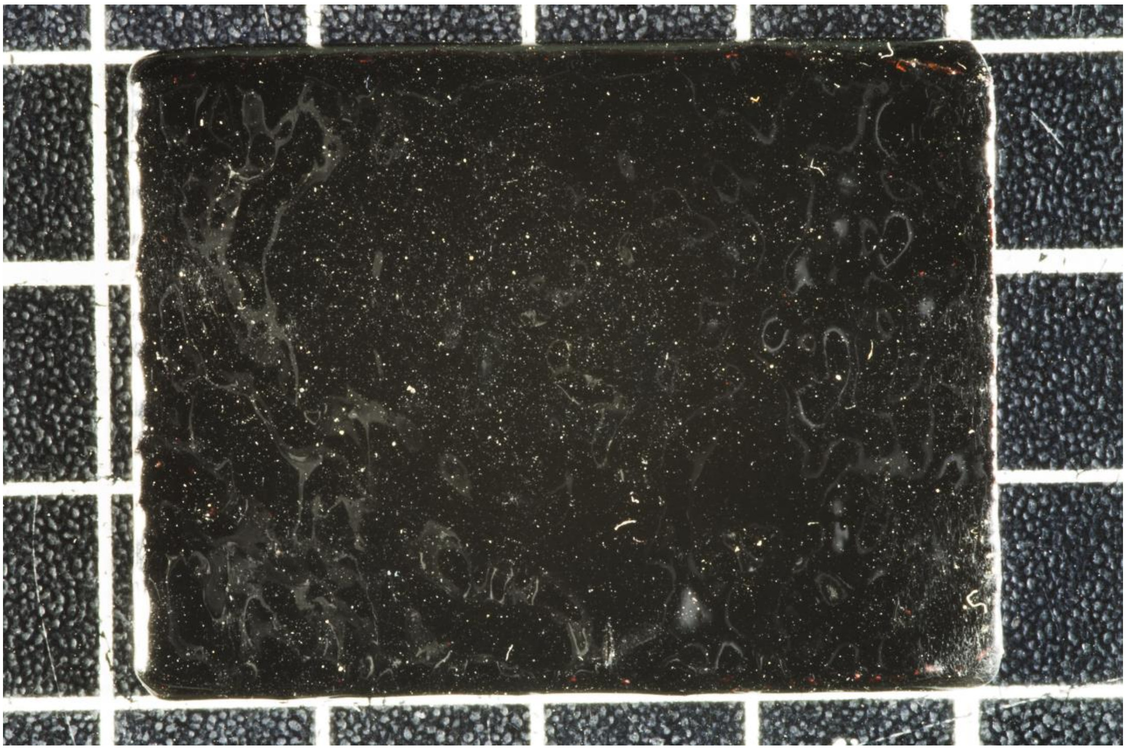


***Figure 5.61** Sample HSII11 showing adhesion of particulates to the surface of System B samples (scale of background scale 10mm between white lines).*

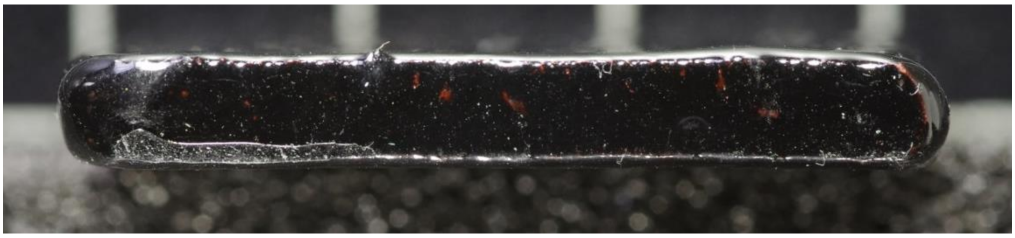


***Figure 5.62** Sample HSII17 after exposure to 90%RH showing particulate pickup and run back of top coat from edges and peaks (sample area shown 30mm x 4mm).*

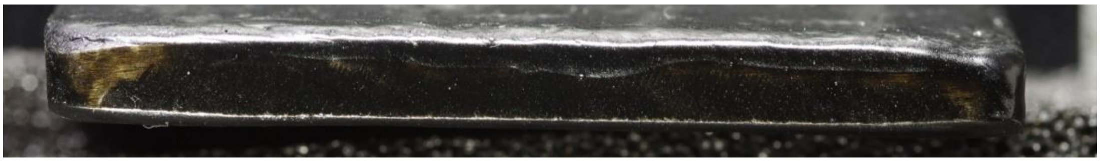


***Figure 5.63** Sample HSII26 after exposure to 90%RH for 540 days showing no visible corrosion even where coating build is very low on edges (sample area shown 40mm x 4mm).*

5.3 Comparing sample materials

Comparison of railing and gasometer sample material is permitted using the corrosion rate data for the aluminium oxide Sa2.5 blasted samples of both materials. The railing wrought iron demonstrates a higher corrosion rate overall and a greater range of values but ranges overlap between the two materials. Boxplots of oxygen consumed and iron converted (assuming [6] is the predominant reaction) are given (Figs 5.64, 5.65).

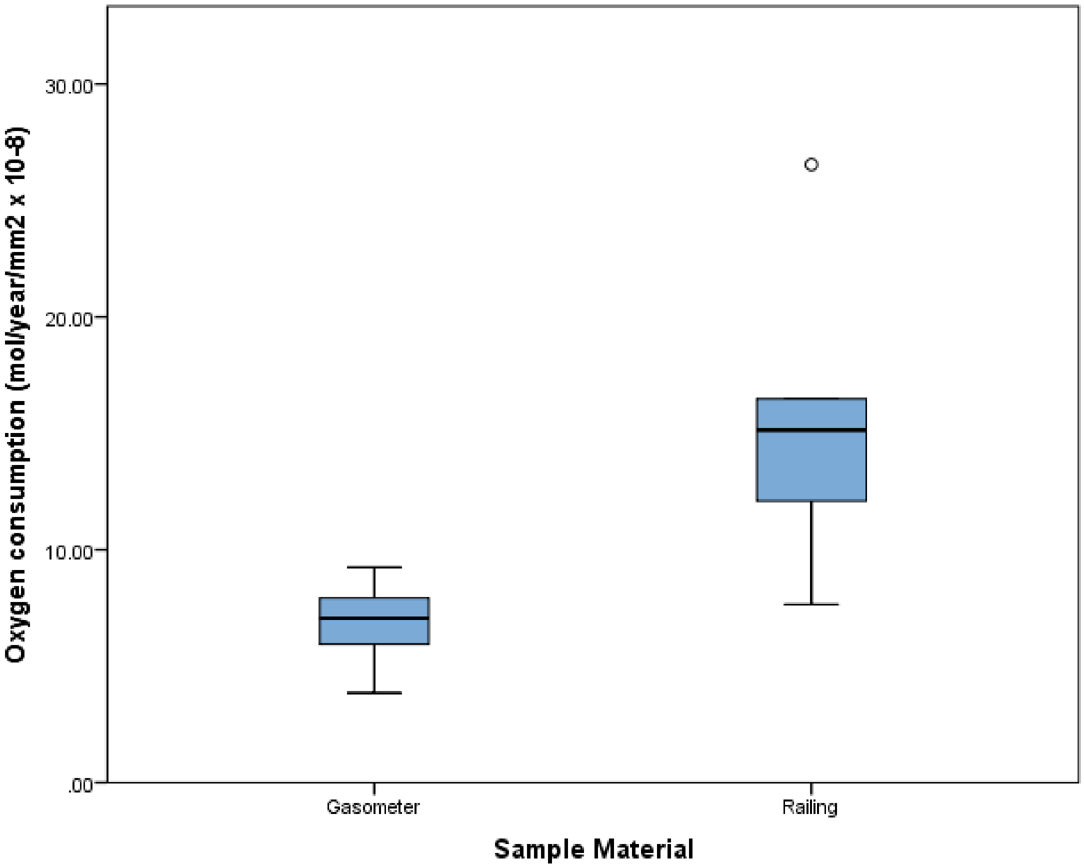


Figure 5.64 *Boxplot showing oxygen consumed by railing and gasometer wrought iron samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

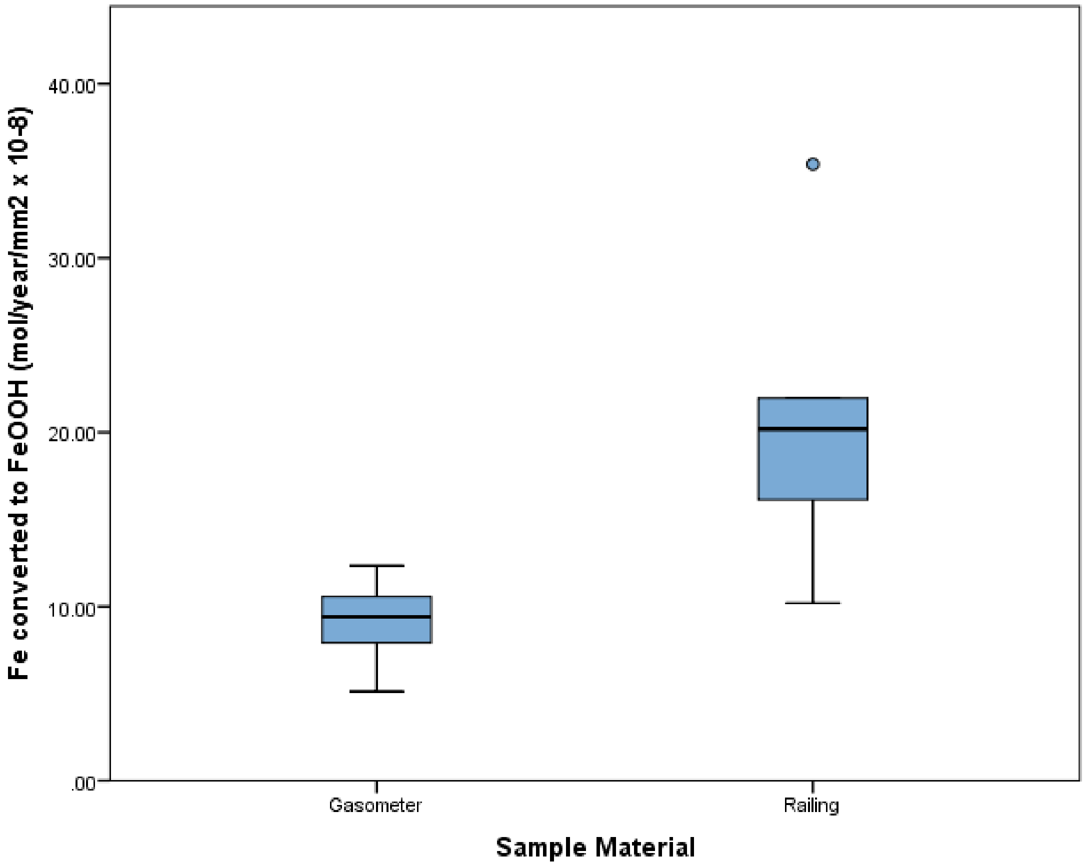


Figure 5.65 *Boxplot showing theoretical metallic iron converted to FeOOH by railing and gasometer wrought iron samples (mol/year/mm^2 x 10^{-8}) as averaged over test period. The box represents the interquartile range, the horizontal line within the box denotes the median and the upper and lower whiskers show the maximum and minimum values. A circle represents an outlying value (lying between 1.5 and 3 times the interquartile range from the upper or lower quartile) and an asterisk represents an extreme value (more than three times the interquartile range from the upper or lower quartile).*

6 Discussion

6.1 Surface Preparation Methods

6.1.1 Grading rust by pictorial standards within heritage contexts

Within heritage conservation it is challenging to define end points for cleaning methods that can be applied across the sector for specifying treatment methodologies to contractors. Swedish Standard SIS 05 59 00 (Standardiseringskommissionen i Sverige et al. 1980) and BS EN ISO 8501-1:2007 (British Standards Institute 2006/2007) specify surface preparations necessary for the protective performance of coatings by determining the preparation end point visually using pictorial grading relative to the original condition of the metalwork. Since they are based on modern steels, pre-treatment surfaces are categorised according to their degree of pitting corrosion. These standards can be used to classify test samples since they employ preparation methods that match those used here: blast-cleaning, hand and power tool cleaning and flame cleaning from four pre-preparation rust grades. However, their use offers challenges for practitioners treating historic wrought iron, which is likely to display more advanced corrosion that is lamellar (Fig. 2.13) rather than the pitting normally evident in the modern steels used to create the standards. How an untreated rusted surface is graded using the standard will have a direct impact on judging the surface aesthetic used to decide the end point of a preparation method (British Standards Institute 2006/2007). While this undermines the value of the pictorial references provided in the standard, because of their limited relevance to wrought iron, in practice, application of an international standard is expected of contractors fulfilling specifications for treatment of wrought iron within the heritage sector.

The importance of using visual comparators to describe the level of preparation attained is underlined by the broad similarity in appearance of the samples prepared here. Differentiation is clearly difficult using only written descriptors therefore an internationally accepted standard provides a base line that can be used comparably across the heritage sector. Despite its limited relevance to the wrought iron, it enables clear specification for contractors and offers comparability between experimental studies carried out within the heritage sector. The grade within the standard that offers the best match for historic wrought iron is D *'Steel surface on which the mill scale has rusted away and on which general pitting is visible under normal vision'* (British Standards Institute 2006/2007). The severe limitations of using BS EN ISO 8501-1:2007 illustrate that employing a dedicated classification based on wrought iron in heritage contexts would be preferable. Developing such a standard may be a consideration for the future, since the wrought iron heritage bank is growing and presents ever greater preservation problems that require predictive management. Generating the standard would be challenging as a corrosion classification would need to be developed from samples subjected to real-time aging and this may take tens of years.

6.1.2 Classification and comparison of prepared surfaces

Using the un-cleaned control sample as a comparator to identify the end point of the surface preparation methods, macro and microscopic investigation of surfaces reveals significant changes have occurred (Fig. 5.9, Table 5.2). Glass beads and aluminium oxide blasted surfaces produce the most change by removing the oxide layer entirely. This correlates to grade D Sa 2.5 *'very thorough blast-cleaning'* or D Sa 3 *'blast-cleaning to visually clean steel'* being free of visible oil, grease, dirt, mill scale, rust, paint coatings and foreign matter and having a more or less uniform metallic colour (British Standards Institute 2006/2007).

Crushed walnut blasted surfaces are noticeably darker in appearance than the un-cleaned controls due to exposure of the dense, coherent magnetite (diffraction code 01-080-0390) layer following removal of overlying loosely adhering and powdery corrosion products and any vestiges of coatings. The outcome corresponds to D Sa 1 *'light blast-cleaning'* being free from visible oil, grease, dirt, poorly adhering mill scale, rust, paint coatings and foreign matter but retaining the closely adhering mill scale (British Standards Institute 2006/2007).

Samples prepared by sodium hydroxide immersion followed by manual wire brushing are markedly more polished and lustrous than the un-cleaned samples. Powdery corrosion products and remains of coatings have been removed and a coherent corrosion product layer is the end point. The surface preparation level corresponds to D St 2 *'thorough hand and power tool cleaning'* being free from visible oil, grease, dirt, poorly adhering mill scale, rust, paint coatings and foreign matter (British Standards Institute 2006/2007).

Flame cleaning causes the least change in some respects. No residues of coatings remain but the surface retains powdery corrosion products. A change in colour is noticeable; the corrosion products have gained a brighter, orange-red hue. The preparation level cannot be said to correlate to D Fl as it is not free from mill scale and rust, possibly due to wire-brushing being manual rather than by the specified power tool procedure in the standard (British Standards Institute 2006/2007). The British Standards relate to modern steels and the mill scale referred to is the oxide layer produced quickly during hot rolling which is reported to be loosely adherent in the long term and prone to cracking and flaking if the metal flexes (British Standards Institute 1998). The corrosion products existing on historic wrought iron may have been produced over long periods and can be closely adhering and relatively stable physically.

6.1.3 **Morphological interpretations**

6.1.3.1 *Blasting techniques*

Spherical glass bead media peen surfaces to produce a satin finish with undulations that are visible at high magnification (Fig. 5.9). This contrasts with the matte surface of the aluminium oxide blasted samples caused by the angular roughness that is evident under high magnification. Both glass beads and aluminium oxide removed all oxide that was visible to the naked eye. The crushed walnut blasted surfaces retain a coherent oxide layer but have lost their paint residues. This oxide layer shows a degree of surface roughness and some angularity which is due to plate-like laminations rather than a micro roughness produced by the cutting abrasive action of impinged media, as with aluminium oxide blasting. Since the hardness of glass beads on the Mohs scale (6) is similar to magnetite (5.5-6.5), corrosion product removal occurs at a slower rate than with aluminium oxide media, providing less danger of underlying metal removal. This degree of control is attractive for heritage practitioners but is less cost effective in terms of operator time and materials. In contrast, the hard, angular aluminium oxide (8-9 on Mohs scale) cuts the surface of the corrosion products on impact, creating a more roughened, angular surface profile. This requires control and vigilance to prevent it removing underlying metal substrate. Despite their angularity, the low hardness (3-4) of crushed walnuts limits their effect to removal of unsupported laminations, powdery corrosion products and polymeric coatings. This controlled and less aggressive nature of crushed walnut is reflected in its industrial use for polymer preparation and in heritage conservation for surface cleaning of copper alloys (Lins 1992).

6.1.3.2 *Sodium hydroxide immersion with manual wire-brushing*

The sodium hydroxide solution (1.25M) solvated the polymeric coatings on the surfaces of the samples but the corrosion products remained insoluble at this pH (Cornell and Schwertmann 2003). Immersion facilitates the removal of powdery and loosely adhering oxides by wire-brushing, producing a surface that appears polished to the naked eye and relatively flat and smooth under high magnification. The areas of slight roughness bear some similarity to the plate-like laminations visible on the crushed walnut and flame cleaned samples with minimal disruption of the surface.

6.1.3.3 *Flame cleaning with manual wire-brushing*

The polymeric coatings adhering to the samples were removed by combustion during flame cleaning. Removal of large laminations of corrosion products by the abrasive action of vigorous wire-brushing was possible but both powdery and adherent corrosion products remain clearly visible. Under high magnification the surface appears rough in a manner similar to the crushed walnut blasted surfaces. The oxide layers are fractured, possibly by differential expansion of metal and oxides during heating leading to loss of laminations. Micro-cracks are visible in some areas and break-up of the oxide layers is evident in section (Figs 5.9, 5.28).

6.1.4 **Suitability of surfaces for application of protective coatings**

Removal of corrosion accelerating contaminants and creation of a mechanical key for adhesion through roughening of the surface are critical for performance of protective coatings on prepared substrates (Higgins et al. 2010; Funke 1985). Of the treatments tested here, blasting with glass beads or aluminium oxide either to Sa 2.5 or Sa 3 is likely to advantageously remove the most contaminants, due to the thorough removal of corrosion products. The angular roughening of the surface profile evident on aluminium oxide blasted surfaces offers better adhesion relative to the undulating profile of glass beads peened surfaces.

Pull-off testing of coatings on blasted and un-blasted surfaces report un-blasted surfaces had the lowest adhesion strengths, with failure of coating adhesion on blasted surfaces occurring between or within coating layers rather than between coating and substrate (Momber and Wong 2005) as was found in this study. However, large peak-to-trough height differentials on surfaces allow rogue peaks to penetrate the coating leading to holidays (Higgins et al. 2010). Clearly the dry thickness of a coating and its application rheology will be of importance in relation to the impact of peak height on coating performance. For aesthetic reasons, the heritage sector often utilises thin, low concentration and transparent acrylic coatings to protect surfaces (Siatou et al. 2007), which means the deep keying supplied by aluminium oxide may prove a challenge to producing a continuous coating with an even thickness, as relatively peak height will be large in proportion to coating thickness. This merits further study as it has major impact on matching coatings to surface preparation and is an area that has received no research in heritage contexts.

Although no impacted particles of blast media were identified on SEM images of prepared samples, this effect has been noted in unpublished tests commissioned by Historic Scotland (Lyn Wilson *pers. comm.*). Blasting angle was modified here to minimise occurrence of impacted media but were this not possible in practice, residual blast media may have a negative effect on coating adhesion.

Problems arise with the techniques which retain the oxide layer, as they are incapable of producing the minimum Sa 2.5 preparation level generally required by manufacturers of coatings that are not formulated specifically for surface tolerance. Removal of the coherent oxide layer is not always either ethically or aesthetically desirable in a heritage context and its retention is not an uncommon requirement. Of the three techniques retaining oxides within this study, blasting with crushed walnut and flame cleaning appear to produce surfaces offering more mechanical keying for adhesion, although this effect may be reduced by the powdery oxides remaining on the flame cleaned samples producing future failure in adherence of the corrosion layer. The smooth and polished surfaces of the sodium hydroxide immersed samples have little potential for mechanical keying but removal of powdery corrosion products may mean fewer contaminants to promote corrosion under coatings and adherence of the corrosion products subjectively appears to be better than for flame cleaning. The un-cleaned surfaces of the controls with powdery, laminating corrosion products and vestiges of previously applied coatings are inappropriate for direct application of a coating due to a plethora of disadvantages that include: unevenness, poor intra surface adhesion, residual contaminants, hydration of oxide layers and ongoing corrosion.

The pictorial standard for flame cleaned surfaces states that flame cleaning must be followed by power tool wire-brushing to remove the products of flame cleaning, as hand wire-brushing does not prepare the surface satisfactorily to receive protective paint coatings (British Standards Institute 2006/2007). For reasons of practicality, manual wire-brushing after flame cleaning was investigated here, since it has anecdotally been found to be common practice in heritage ironwork conservation (see 4.2.8). The presence of powdery corrosion products on surfaces after such cleaning lends weight to the assertion that this is not satisfactory preparation before application of paint.

6.1.5 Practical considerations in application of preparation methods: heritage context

6.1.5.1 *Blasting with glass beads, aluminium oxide and crushed walnut shell*

These three blasting techniques were similar in their application, equipment needs and practical considerations. Blasting within a cabinet is a relatively controlled process with detritus of operation largely contained, as is blasting of large objects in a workshop. In situ blasting requires a system by which spent media, corrosion products and paint are collected and cleared from the site. The cost, practical and financial considerations of in situ blasting often preclude their use in heritage contexts where resources are often severely limited.

Control of parameters such as angle of nozzle to and distance from surfaces is readily achievable with small, flat samples in the blasting cabinet, making this method ideal for portable heritage structures. It would be difficult to accomplish in situ for large, complex structures within heritage, although garnet blasting to Sa2.5 was successfully used by Eura Conservation to prepare the surface of Brunel's ship ss Great Britain (Watkinson and Tanner 2008). Additionally, the morphology of heritage objects may make it difficult to remove paint layers and corrosion products from intricate and inaccessible areas of a structure by blasting, although this is equally true for other preparation methods. The pressures involved have potential to buckle material of thin section or destroy heavily corroded and weakened heritage iron that it is normally desirable to retain.

Health and safety concerns exist relating to exposure of the operator to airborne particulates and to disposal of blasting detritus. Crushed walnut shell has the potential to cause allergic reaction and the larger, angular particles require use of heavier weight protective gloves. Considering these factors it appears that blasting is an ideal preparation method for use on smaller heritage objects, where total removal of coatings, corrosion and surface finish is acceptable, with execution occurring in controlled workshop environments. Its use in the field may be suitable or even essential on large projects such as ss Great Britain but this is at the expense of high cost and less controlled application, making it appropriate for large, well-funded in situ projects. Cost of the method may be a movable point when the input of operator time is considered.

6.1.5.2 *Immersion in sodium hydroxide solution and wire-brushing*

Immersion of samples in sodium hydroxide is a simple, controlled process in the laboratory but this technique requires disassembly of structures, removal from site and access to a sufficiently large dipping tank for immersion. In situ application may occasionally be possible and techniques employing poultices could be considered but rinsing to remove sodium hydroxide solution is necessary and must be planned for from financial, disposal and health and safety viewpoints. Similarly to blasting techniques, sodium hydroxide seems to be better suited to the controlled environment of the workshop for heritage contexts.

6.1.5.3 *Flame cleaning*

This is a far less controlled and more operator dependent preparation method when compared to other techniques examined here. Maintaining surface temperatures, torch to surface distance and even distribution of heat, along with assessing the end point of the process, are entirely qualitative decisions with large operating parameters based on operator experience and interpretation. How reproducible this preparation technique could be for heritage objects requires further research that examines how differing temperatures, time of treatment, operator identity, surface morphology and oxide transformation influence the consistency of the preparation end point. The importance of form in heritage metalwork and often inherent object fragility mean flame cleaning is not suitable for iron of section less than 5mm, due to deformation risks (heritage ironworkers *pers. comm.*). This is clearly not a technique to be applied by inexperienced operators. Major advantages for contractors are its portability for in situ work, low cost and conformation to an international standard and the assurance that this appears to offer; disadvantages include hazards from large scale combustion of existing paint layers, especially as lead based paints are often present within heritage coatings.

6.1.6 **Success and practicality criteria**

The advantages and limitations of the preparation methods have been discussed but a useful summary is perhaps to consider how the techniques comply with practitioner and specifier criteria for practicalities and success (Table 6.1).

Criteria	**Compliant methods**
Removal of oxides and contaminants	Glass beads blasting Aluminium oxide blasting
Retention of oxides	Crushed walnut blasting Sodium hydroxide immersion/wire brushing Flame cleaning/wire brushing
Keyed surface for coating adhesion	Aluminium oxide blasting Glass beads blasting (to an extent)
Reduced corrosion rate of substrate	Sodium hydroxide immersion/wire brushing Crushed walnut blasting
Minimal waste produced	Flame cleaning/wire brushing
On site treatment possible	Glass beads blasting Aluminium oxide blasting Crushed walnut blasting Flame cleaning

Table 6.1 *Compliance of surface preparation methods with practitioner/specifier criteria.*

6.1.7 Oxygen consumption rates of prepared surfaces

All samples consume oxygen and show a decrease in oxygen consumption rate over time (Figs 5.10-5.15). Oxygen consumption rates can be examined via the changing gradient of the average trendline for each preparation method (Fig. 5.17). This is done by using visual analysis of consumption graphs based on dividing the trend line into an initial period of 0-12 days (0-20 for un-cleaned samples), secondary period of 19-103 days (20-104 days un-cleaned) and final period of 103-338 days (104-257 days un-cleaned). Un-cleaned sample corrosion rate testing was conducted separately, hence discrepancies in gradient analysis periods. As might be predicted, all surface preparation methods show highest average consumption rates during the initial exposure period when the maximum area of freshly exposed metal is present and available for oxidation. Once oxides form a degree of passivation ensues, reducing corrosion rate.

6.1.7.1 *Total consumption over study period*

Clear and significant differences in oxygen consumption rate can be identified between a number of preparation methods using average oxygen consumption (mol/year/mm^{2}x10^{-8}) of sample for each preparation method, with the un-cleaned samples as a baseline for comparison (Table 5.4). No significant difference could be determined between aluminium oxide and glass beads blasting methods or sodium hydroxide and crushed walnut blasting methods, which is evident when examining box plots (Fig. 5.18). Removal of oxide layers to reveal the metal surface, using glass beads or aluminium oxide blasting, produced higher average oxygen consumption than the un-cleaned control. This is likely due to the exposure of the metallic surface and its unevenness offering a relative increase in surface area and a large reaction platform of exposed metal still populated by corrosion accelerators. In contrast, there is a closely adhering, coherent oxide layer overlying the metal surface of the untreated sample but this also retains all corrosion accelerators. Initial high oxygen consumption of exposed metal surfaces is expected and is followed by slowing as corrosion products develop (Fig. 5.17). The higher average oxygen consumption of aluminium oxide blasted samples, relative to those blasted by glass beads, may be due to a larger surface area produced by the rougher surface finish on the aluminium oxide samples. Upon termination of the tests both aluminium oxide and glass bead sample sets had developed new corrosion products concentrated in areas previously pitted during atmospheric exposure of the railing and along slag planes (Fig. 5.19). This is likely due to the low pH anodic centres expected within pits and the potential difference between slag and iron (Scott 1989).

Both crushed walnut blasting and sodium hydroxide immersion with wire brushing decrease average oxygen consumption relative to the un-cleaned samples average. They show negligible oxygen consumption beyond 50 days (Figs 5.12, 5.13, 5.18). Treatment with sodium hydroxide solution has long been reported to inhibit iron corrosion (Mayne and Menter 1954; Mayne et al. 1950; Turgoose 1985), which may explain the reduction in corrosion rate recorded. For crushed walnut it may be that the impact of the blast media further compacts the coherent corrosion product layer visible on the sample surfaces post-cleaning, enhancing protection of underlying metal substrate and delivering hydrophobic effects from the drying oils in the nut shells. These oils cross link to produce films (Mills and White 1987), whose hydrophobicity is evidenced in their traditional use for paint media. Developing even a thin non continuous drying oil layer offers potential to hinder moisture and oxygen ingress to anode sites at the metal surface. The dark colour of the surface post-preparation may be due to oils and disappears post-corrosion due to formation of new corrosion products (Fig. 5.9).

Despite, or because of, the retention of closely adhering corrosion that must also retain contaminants beneath it, both these preparation techniques reduce corrosion rate relative to the un-cleaned control (Fig. 5.18). However, their lower oxygen consumption rate may simply relate to the arithmetic of there being a smaller reactive surface area due to retention of coherent corrosion product layers that hinder ingress of oxygen and moisture. The potential impact of a drying oil layer could be examined by using aluminium oxide blasting to remove all corrosion products, then impinging crushed walnut shells onto the surfaces of the samples. Oxygen consumption rates could then be compared to those of aluminium oxide prepared samples which were not subsequently subjected to crushed walnut blasting.

Flame cleaned samples show a considerably higher oxygen consumption rate than the un-cleaned samples (Fig. 5.18). While macroscopically the extent and form of corrosion product on flame cleaned samples was least changed relative to un-cleaned surfaces, showing only colour difference, at high magnification a fractured and micro-cracked surface is evident (Fig. 5.9). SEM images of the cross section of flame cleaned samples shows fragmentation of the corrosion product layers (Fig. 5.28). While differential expansion of oxides and metal substrate are used to describe the mechanism by which oxides are removed from the surface, it may also cause fracturing and cracking, which then offers pathways to oxygen and water ingress and subsequently corrosion. These imperfections make it difficult to understand the popularity of flame cleaning and emphasise the need for much more quantified assessment of flame cleaning as a preparation method. This is further evidenced in the practitioner methodology. Evidence based support for the efficacy and advantages of flame cleaning are hard to find.

6.1.7.2 *Practitioner flame cleaning*

Results obtained by the laboratory flame cleaning procedure are reinforced by the oxygen consumption rates of the practitioner flame cleaned samples. Although the laboratory method was verified by a practitioner as being representative of the field procedure, other practitioners understandably questioned the method when results demonstrated a surprisingly high oxygen consumption/corrosion rate.

There is no significant difference between the corrosion rates of the samples cleaned by practitioners PA and PB. The range of rates is similar in both cases. Corrosion rates of the samples prepared by practitioner PC are significantly lower than both PA and PB. All three practitioners employed slightly different methods with parameters most likely to impact corrosion rate identified as the nature of the torch (oxypropane or oxyacetylene), the temperature of the metal during cleaning and the time for which the flame was applied to the metal (see Table 4.3).

Practitioners PA and PB used oxypropane torches with oxygen boost setting to increase flame temperature. Practitioner PC used an oxyacetylene torch with no oxygen boost. Oxyacetylene flame temperature is generally higher than oxypropane. Flame application time was greatest for PC (50-60 seconds contact time with breaks to wire brush), slightly less for PA (20-30 seconds) and least for PB (<10 seconds). All practitioners had similar parts of the flame in contact with the sample surface (Figs 6.3, 6.4, 6.6).

Temperature of the metal during flame cleaning is likely more important than time of flame application. None of the practitioners could state the metal temperature during cleaning with confidence. Colour of the metal is given to be a rough measure of temperature (Uddeholm n.d.) and the samples prepared by PA and PC both achieved a dull blood red/cherry red state (Table 4.3, Figs 6.2, 6.7) estimated to be c.550-650^{o}C (Uddeholm n.d.). Samples prepared by practitioner PB remained grey throughout, likely below 300^{o}C. Practitioner PA estimated a temperature of 500^{o}C which is likely lower than that actually attained. PC estimated 700^{o}C, probably an overestimation, and PB c.100°C which may well be approximately correct as it was lower than the temper colour range. There may be corrosion product transformations occurring at the elevated temperatures. Transformation of goethite to haematite has been reported at 240 – 250°C (Ruan et al. 2002) and lepidocrocite to maghemite at c.200°C which is metastable and transforms again to haematite at c.500°C (Gehring and Hofmeister 1994). Transformation of oxides may explain the bright red corrosion products seen within a minute or so of flame cleaning a sample (Fig. 6.8).

Given that the time of application of flame to the surface was different for all practitioners and temperature of the metal was similar for PA and PC but different for HI, the parameter which separates PA and PB from PC is the nature of the torch. Practitioners PA and PB used oxypropane torches (Fig. 6.4). It should also be noted that this corrosion rate tested an unreal scenario. None of the practitioners would have flame cleaned wrought iron without immediately applying a coating to the surface, be that linseed oil, a rust converter or a polymeric coating.

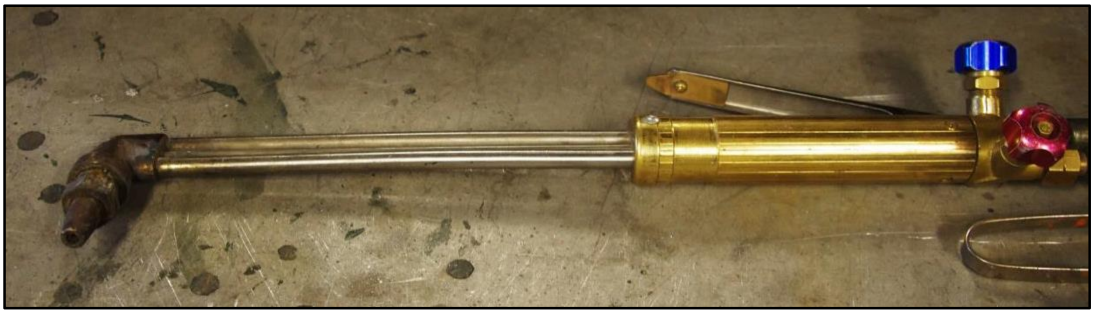


Figure 6.1 *Oxypropane torch used by practitioner PA.*

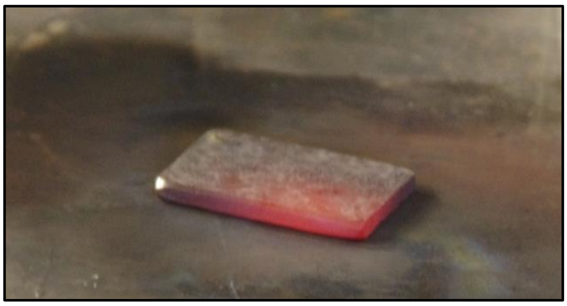


Figure 6.2 *Dull red glow of sample flame cleaned by practitioner PA.*

Figure 6.3 *Position of the flame relative to the sample during flame cleaning by practitioner PB.*

Figure 6.4 *Luminescence of coating and oxide vestiges under flame (practitioner PB).*

Figure 6.5 *Wire brushing of flame cleaned sample by practitioner PB.*

Figure 6.6 *Position of the oxyacetylene torch relative to the sample during flame cleaning by practitioner PC.*

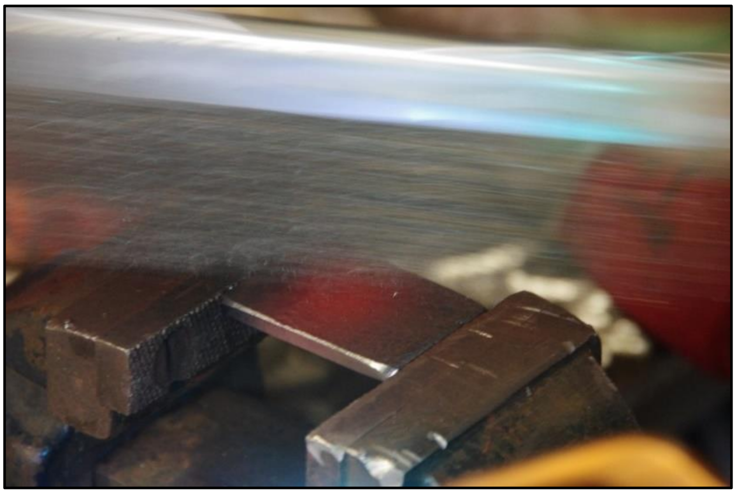


Figure 6.7 *Dull red glow of wrought iron during flame cleaning by practitioner PC.*

Figure 6.8 *Characteristic bright red oxides forming developing 1-2 minutes after flame cleaning on all samples (uncleaned sample top left for comparison).*

6.1.8 Flame cleaning in practice

Practitioner flame cleaning is carried out in an ad hoc manner with a range of methods employed and different philosophical approaches. Torch choice may be based on availability and cost. Oxyacetylene is more costly than oxypropane. Use of the oxygen boost cutting flame with the oxypropane torch was deliberate to increase flame temperature and burn off paint layers more quickly. Flame application time must relate to extent of corrosion product and amount and nature of existing coatings but also to the philosophy of the practitioner. PB was concerned with conservation ethics, preserving historic evidence within the metallographic structure and the idea that the metal last attained red heat during forging. This concern led to the shortest duration of cleaning and lowest metal temperature. Neither PA nor PC considered negatives of heating the metal in relation to the material or principles of conservation. This divergence, one practitioner using ethics to control end points and two others using appearance during the process, apparently ignores any interpretation or conception of physical or chemical outcome for the metal and relation to application of coatings. Additionally, and perhaps cynically, it may be that flame cleaning is carried out to ‘tick a box’ for procedure and evidence base in relation to coating procedure and any future failure.

A high level of experience and knowledge of the materials and their properties as related to the task in hand does not prevent a ‘technician approach’ to work. Unless an agreement is in place for maintenance work by the same practitioner, an individual may never be in situ to judge long term implications of decisions and practices in cleaning and coating ironwork. Training directs practitioner thought processes; the conservation trained individual was more thoughtful about impact of decisions on retention of historic evidence, for example. It may be through training that a synergy of practical experience and understanding of chemical and physical processes can be produced both to improve practice and researcher knowledge. Practitioners are an invaluable source of information regarding wrought iron, its properties and responses to treatments.

6.1.9 Interpolation to develop context

By linking the morphology of the surfaces produced by the selected preparation methods to their oxygen consumption rate in high humidity, defined as a proxy for corrosion, a more informed approach to devising coating systems for heritage iron is possible. Whilst no tests examining the adhesion of coatings to surfaces were carried out, it is possible to use surface morphology to predict that aluminium oxide and glass bead blasting potentially offer the best keying surfaces for coatings. There is little to choose in terms of keying morphology for the walnut blasted samples and the flame cleaned samples, with both offering less keying opportunity than either aluminium oxide or glass bead blasting. Sodium hydroxide appeared to offer the fewest keying opportunities but this must be balanced against the often powdery finish on the flame cleaned samples, which is likely to interfere with adhesion. Similarly, the possible impact of oils delivered by walnut media on adhesion of coatings must be considered, although it requires further study.

Linked to these predictions of coating performance relative to keying onto surfaces must be the response of the surfaces themselves to high relative humidity. Should a coating applied to each surface offer exactly the same transmission of moisture and oxygen then this study indicates that sodium hydroxide and walnut blasted surfaces can be expected to corrode more slowly than glass bead blasted surfaces, which will corrode more slowly than aluminium oxide blasted surfaces with flame cleaned surfaces offering the worst corrosion rate of the five treatments. It is tempting to translate this into an estimation that slower corrosion rate of the samples tested here mean that a coating would remain fit for purpose for a longer time period on the less reactive substrate surfaces, thus offering better cost benefit. However, there are multiple variables that relate to coating performance. In this instance, the degree of disruption to the coating caused by the corrosion forming on the metal surface may influence its performance and adhesion at an early stage of the corrosion process. This may cause corrosion rates at the metal surface to diverge from those identified when testing surfaces without applied coatings. Also, the initial adhesion of the coating to the surface may have a major influence on how any corrosion impacts on the coating above it. Only further testing could examine these factors and other variables to add to understanding that could build a clearer picture of the complex relationships between coatings and surfaces. This study has effectively examined one fixed condition context, changing the context may well change the order of comparative performance. It is these multiple scenarios that must be tested which make development of guidelines and a model so difficult.

6.2 Protective Coatings

The array of factors in decision-making for coating selection was discussed in 3.4. These are revisited in the light of the coating performance test results to discuss their impact on decision-making and how the coatings tested here fare in relation to these concerns. Emphasis is on the thought process behind the decision-making and the contribution of empirical evidence and qualitative understanding of coating properties and practicalities (Tables 5.6, 5.7) to guiding decisions. Anti-corrosive performance of a coating in laboratory testing is not the sole factor in selection. Ultimately, long term success is likely due to a complex web of factors including achievability of a defect-free coating in field application, compatibility of the coating with the substrate and its dynamic responses to environments, its maintainability and its fit to the historic context in addition to its anti-corrosion credentials.

It is assumed that in many instances the decision maker is not a specialist in coating ferrous metals and may not be trained in conservation principles and heritage context. The report of flame cleaning by heritage ironworkers highlights the variation in understanding of materials and their properties, the influence of treatment processes on subsequent survival of materials, and the principles of preservation of evidence and retention of original material. It also underlines the benefits of experience and anecdotal evidence of successes and failures where much of the following discussion relies on laboratory testing and manufacturer claims.

This discussion centres on selection of a coating system and is separate from the discussion of surface preparation methods. In reality, the two are interrelated. The extent of surface preparation may be predetermined and coating selection must aim to find the most appropriate system for the surface, or vice versa. Table 6.2 offers an overview of the coating systems tested highlighting features relevant to the discussion.

	System A	**System B**	**Coating C**
System	Primer (2 coats) Build (2 coats) Topcoat (2 coats)	Primer (2 coats) Topcoat (2 coats)	Single coating (2 coats)
Surface Preparation	Blasting Sa2.5	Blasting Sa2.5 or wire brushing and rubbing with coarse abrasive paper	Wire brushing
Surface prep contractor required?	Yes	Yes	No
Coating contractor required?	Likely for best results	No	No
Cost	£12.50/m^2 coating + blasting contractor + waste disposal + coating contractor	£11/m^2 coating + blasting contractor or emery paper + waste disposal + paint brush	£7/m^2 coating + wire brush + paint brush
Loss of original material?	Yes	Yes	Minimal
Availability	Online	Online/DIY outlet	Online/DIY outlet
Application	Brush/Roller/Spray	Brush	Brush/Spray
Appearance	Plastic High build	Glossy Medium build	Matte/satin Low build – surface profile evident
Colours	Vast range BS 381 and RAL colours	6 traditional colours	Satin – black/white Hammered – 8 colours Smooth – 12 premixed/26 store mixed colours
Recommendations	Forth Rail Bridge ss Great Britain Compliance with British Standards Railtrack Ministry of Defence Highways Agency	Household name	Household name

***Table 6.2** Summary of features of coating systems tested.*

6.2.1 Cost

This is a critical factor in the planning of many projects yet there is limited difference between these coatings on face value. System A is more expensive per m^2 being formed of three coatings each applied in two coats but the cost of the coatings per litre is slightly less than System B and Coating C. Likewise, there is little to choose between System B and Coating C based on coating cost per m^2 although differences of a few pounds per square metre become more important when calculated over a large area.

There are a few main differences in cost between the coating systems when considered in detail. First, the requirement to blast surfaces to Sa2.5 or near white metal for optimal performance of System A necessitates use of specialist equipment and likely employment of a contractor to carry out the work. If the chosen surface preparation for System B were wire brushing and rubbing down, this could be carried out by a non-specialist but is likely to be time consuming, adding an employee time cost. The minimal surface preparation for Coating C likely incurs the lowest cost.

Second, the application of the coating has cost implications. If spraying were chosen as the application method for System A, further equipment and contractor costs could be expected. System B and Coating C are readily applicable with care by non-specialists. Brushes can be cleaned readily with white spirit and reused. The two-pack nature of System A coatings (the need to make up in a correct ratio and the changing properties of the coatings as they react in the pot (see 5.2.3)) make application more difficult and may necessitate using a specialist contractor. If System A is applied by brush by a non-specialist, painting equipment (e.g. brushes and pots) should be considered disposable, adding to the cost.

A cost implication arises from tin sizes available for each coating. System B coatings and Coating C are available in volumes starting from 250ml. The smallest readily available for System A coatings is 5 litre. If the area to be coated is small, the large tins of System A may be a disincentive. Given the lifetimes to maintenance discussed below, it is unlikely that remainders of the unused coatings would retain their quality until required for maintenance coating.

6.2.2 Availability

System B and Coating C are produced by a household name manufacturer and readily available off the shelf at DIY outlets. This offers the benefits of browsing products on a shelf, asking an assistant for advice and easy access should more coating be required unexpectedly and in a hurry. Availability at well-known outlets lends a feeling of popularity and ‘tried-and-tested’ to these products. Alternatively, the ‘household’ nature of the manufacturer may seem insufficiently technical and suitable only for domestic scenarios.

System A is available to order online but difficult to source from other outlets. Browsing requires scrolling through internet pages rather than examining tins on a shelf. The tins themselves are clinical, without attractive embellishment or logos. This may be less or more convincing depending on decision-maker mind-set. A technical coating sold on merit not packaging may imply greater efficacy in performance. Advisors are available via a telephone service but there is limited option for face to face discussion. Internet ordering may be ideal big projects requiring delivery of large volumes but difficulties or delays may arise if underestimation means more coating is required to finish the work.

6.2.3 Volumes of coating and numbers of coats

This is standalone but strongly linked to cost considerations discussed above. The greater the mass of coating added, the greater the cost, the longer the time in application and the more disfiguring to fine detail of a surface or structure (Figs 5.34, 5.37). Alternatively, the perception may be that a greater mass of coating affords more protection to the substrate. Either way, there is a clear financial distinction between System A (6 coats applied in total) and Coating C (2 coats applied) and this may be important in selecting between very interventive (System A) and minimally interventive (Coating C) approaches. In performance terms, this links to the protective nature of the coherent and closely adhering oxides retained under Coating C. The surface tolerant coating exploits protective oxides (and any sound existing coatings) which increase the thickness of the effective barrier to water and pollutants driving corrosion without the necessity of multiple coating applications.

System B comprises two coats each of two coatings, offering a compromise with the extra protection of a primer under the topcoat but no build coat. Crucially, any protective oxides are removed before coating. Despite appearing to offer greater protection through an increased number of coats, some protective effect may be lost with the oxide layers relative to Coating C.

Application of each coat is an investment of time and money. If coating is carried out by staff there are salary costs and commitment of time. If carried out by a contractor there is a direct cost of contractor time and inconvenience of contractor presence on site for a longer period. Manufacturers stipulate over-coating intervals for optimum coating cure between coats. A long over-coating interval can delay or extend a project. Coating compatibility may dictate timings; there is an over-coating window after which the polyurethane topcoat of System A will not adhere successfully to the intermediate epoxy build coat (Leighs Paints 2008b). The topcoat must be applied within 7 days of application of the build coat. A coating system requiring multiple numbers of coats may be viewed unfavourably, especially if slow curing or introducing time constraints for application schedules.

Measurements of coating thickness are given in Table 5.8. Overall system build ranges are 210-406µm (System A), 23-98µm (System B) and 11-64µm (Coating C). Ranges are increased by pitted substrate surfaces with greater coating thickness in pits and reduced thickness on peaks due to run back of coating (Fig. 5.42). BS EN ISO 12944-5:1998 gives expected durability of coatings based on surface preparation grade, coating type, number of coats and dry film thicknesses (DFT) of coats and complete systems (British Standards Institute 1998). How DFT relates to corrosion rate of substrates is not explained. With barrier coatings, conceivably the greater the DFT the greater the diffusion pathway for moisture and ions for a given coating. No option correlates exactly to System A but the stated durability of the closest system in urban and industrial atmospheres (category C3 medium) is High which equates to more than 15 years. The closest to System B in the same environment has a Low durability (2-5 years) although none of the DFT values are as low as those recorded with System B. No paint system in the standard has as few coats as Coating C or DFT values lower than 120µm so this must also have a Low durability.

6.2.4 Primers

This links to number of coats and to perceptions. The necessity of priming a surface is a disincentive for some, increasing amount of coating needed and number of coats with cost and time implications as discussed. For others, a primer is attractive implying more adequate preparation and greater overall efficacy of the system relative to a single coating such as Coating C. The term ‘primer’ indicates that the product improves the readiness of the iron to receive the final coating. Implicit is an extra level of care, attention to detail and a better overall finish. It may also improve aesthetic properties such as depth of colour if chosen to complement or enhance the colour of the topcoat. Primers can only be applied with suitable surface preparation; by definition it must be applied to the substrate surface not over existing coatings.

6.2.5 Required surface preparation

Discussed above in relation to cost and time implications, there is also a crucial ethical consideration. Blasting to Sa2.5 (near white metal) produces an effective keying surface for adhesion of coatings and removes corrosion accelerating contaminants but it also removes the oxides which represent original historic material and may be protective. Evidence retained within corrosion layers, such as mill scale, will be lost as the original surface of the metal is removed. Blasting also diminishes metal section and this thinning of the material may reduce structural strength. Although System A replaces some of this with bulk of coating, it is not integral to the core material.

Wire brushing for Coating C does not offer such effective keying for adhesion of the coating but is appropriate for the surface tolerance of the coating, likely preserves much original material and fits with a minimal intervention conservation strategy. Wire brushing followed by coarse abrasive paper rubbing could be a preparation strategy for System B, removing more original material than wire brushing alone but much less than blasting to Sa2.5.

6.2.6 Application

System A is applied by brush, roller or spray. Brush application requires no specialist equipment and is more effective for coating hard to reach areas and convoluted details. Application of System A coatings should be at temperatures of 10°C and above and humidity <90% RH (Leighs 2008 a,b,c) which has implications for in situ application to exterior ironwork during the winter months or wet periods even if the ironwork itself is under shelter. Spray application by a non-specialist is problematic with regions of insufficient coverage likely to have numerous holidays (holes in the coating) (Fig. 6.9) and areas of a structure sheltered by other parts being difficult to reach with the spray. Even with the close contact and attention to detail possible with brush application, areas may be missed and consequent low build afford reduced protection (Fig. 5.45). System B and Coating C can be applied by brush with System B primer also applicable by roller and Coating C by spray. The same considerations apply as with System A. The oil-based coatings are more temperature tolerant at the lower end (being applicable down to 8°C) but have an upper recommended limit of 25°C.

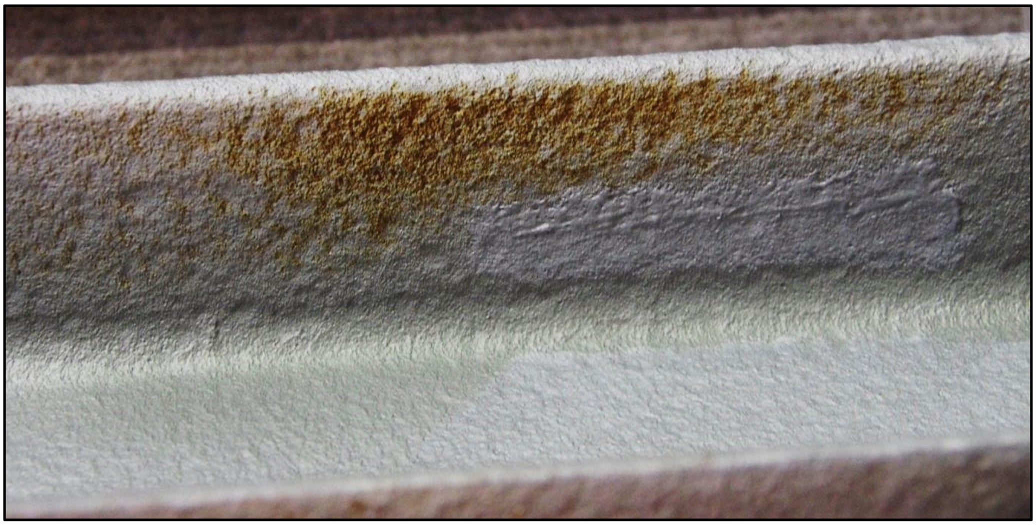


Figure 6.9 *Showing corrosion from pinholes in a sprayed coating.*

6.2.7 Testing quality of application

Paint test equipment can be bought, hired or borrowed to check the quality of the coating application. Dry film thicknesses (DFT) can be tested with a thickness meter such as the DeFelsko PosiTector 6000 to assess compliance with manufacturer specified DFT values. Difficulties arise with pitted and uneven historic wrought iron surfaces leading to regional differences in coating thickness between the peaks and troughs of pitted surfaces.

BS EN ISO 12944-5: 1998 uses nominal DFT to assess thickness (British Standards Institute 1998). This takes an average of the thickness readings across the sampled area. For historic material with extensive pitting and uneven surfaces, this is a misleading measure. Table 5.8 gives the nominal DFT for System B (run-back from peaks present Figs 5.41, 5.42) as 58µm but the lowest DFT measured was 31µm, nearly half the nominal value. For Coating C this is more pronounced with a nominal value of 43µm yet lowest DFT value is 11µm, a quarter of the nominal. Settlement of coatings into troughs and run back from peaks may cause this variable DFT across a surface. Nominal values are dangerous if they mask low values in areas where lack of build means susceptibility to corrosion. Unrealistic expectations of durability and lifetimes to maintenance may result based on comparison of nominal DFT values to manufacturer guidance which assumes flat prepared surfaces. Thus the build and rheology parameters of a coating are likely to have a *very* significant impact on coating performances on heritage wrought iron.

6.2.8 Adhesion of coatings

Adhesion is taken to correlate to effectiveness of protection by the coating. It is tested by the procedure described in 4.3.9.2 according to the standard BS EN ISO4624:2003 (British Standards Institute 2003). The method is straight forward but interpretation of the data is less so. There is no clear consensus on what constitutes a ‘good’ adhesion reading. Generally, the higher the value the better the performance of the coating is assumed to be but this idea has been challenged (O’Donoghue et al. 2010; heritage practitioners *pers. comm.*). As important as the pull-off value is the mode of failure of the system. Possible failure modes are:

- adhesive between primer and substrate;
- adhesive between coatings;
- cohesive within coatings;
- adhesive between dolly adhesive and topcoat;
- cohesive within dolly adhesive;

- adhesive between dolly and dolly adhesive.

Each mode of failure informs on the weakest point within the coating system and the dolly. The value of the pull-off test is the strength of the weakest adhesive or cohesive bond within the system.

Results of pull-off tests for coatings examined here are given in Table 5.9. There is good agreement between the measured values for each coating system. Where values are lower within a group, this correlates with dollies which had fewer points of adhesion between the cyanoacrylate on the dolly and the surface of the coating system. This is a particular problem on the pitted and laminating surfaces common in heritage. Values for System A were higher than System B which were higher than Coating C. This is unsurprising as greater adhesion is expected on blasted surfaces with their improved profile for adhesion (Momber and Wong 2005). Modes of failure for both systems on blasted substrates mean actual values for primer to substrate adhesion must be higher than the pull-off value as there was no failure between the primer and the substrate in either case. System A failure was cohesive within the primer layer. This could be at the interface between successively applied coats of primer but this cannot be determined. High solids, zinc-rich primers contain lower than ideal percentages of binder which reduces cohesive strength (Sørensen et al. 2009, 144). Within System B, failure was adhesive between primer and topcoat. With Coating C, failure was cohesive within the corrosion products. The value for adhesion of coating to corrosion products is higher than the pull-off values. Adhesion values for systems A and B are likely relatively reproducible on different substrate material prepared in the same manner but the values for Coating C must depend on corrosion product nature and will vary between substrate materials.

Holiday testing allows detection of pinholes in a coating which are unprotected areas. The test was not applied to the coatings in this study due to unavailability of a holiday tester. Pinholes are visible on the coated samples (Figs 5.36, 5.39, 5.43) but with a high build system such as System A it is unlikely that pinholes in the topcoat would be detected. The value of multiple applications of coats is that defects are unlikely to overlie one another which reduces the chance of any faults extending from coating surface to metal substrate.

6.2.9 **Aesthetics**

6.2.9.1 *Colour range*

Coating C is available in satin, smooth or hammered finishes. Satin was chosen here as most likely to conform to the historic aesthetic but this version is currently only available in black or white. The hammered finish is available in 8 colours and the smooth in 12 premixed or 26 colours mixed in store. System A topcoat is available in a vast range of British Standard 381 colours and RAL colours. Colour could be tailored perfectly to the particular job and may offset the plastic appearance of the system. System B topcoat is available in six traditional colours allowing some scope for matching to historic paint schemes but not such a tailored approach as System A. The importance of this factor will depend upon expected adherence to historic aesthetic in the project and whether nuances of colour are more valuable than a traditional oil paint finish.

Colour selection also relates to ability to judge quality of coating application. Coating shade should be sufficiently different to the preceding coating in a system to allow visual identification of pinholes and missed areas (Norsok 1999). The number of coats of the topcoat must then account for the need to obscure the colour of the primer or build coat. The colour of the primer relative to the substrate material should also be sufficiently different. Figure 6.10 shows areas of mild steel structural elements missed during spraying of the primer/build and subsequently corroding. Although the missed areas are evident now due to the corrosion products, the contrast between the steel blasted to Sa2.5 and the grey coating may have prevented easy identification during application.

a.

b.

c.

Figure 6.10 a-c *Showing corrosion on mild steel structural elements in areas missed during coating application.*

Pigment volume concentration and type linked to coating colour may also impact on performance by affecting barrier properties, for example. Manufacturers are notoriously tight lipped regarding formulations of coatings so the effects of this are difficult to predict but could be quantified by testing different colours of the same coating.

6.2.9.2 *Appearance and change over time*

The appearance of the coatings as applied to wrought iron can be seen in Figure 5.34. System A is characterised by a high build which obscures surface morphology and may obscure delicate features within a structure. The overall appearance is somewhat ‘plastic’ which is undesirable if conformation to the historic aesthetic is a priority. For the public, the concept of ‘original appearance’ is important as part of the visitor experience. A modern finish spells ‘replica’ to many. Where systems such as this have failed, corrosion has caused extensive staining of lighter colour shades such as that tested here (Fig. 6.11). Epoxy resins are susceptible to ‘blooming’ with exposure to UV light and the polyurethane topcoat applied here aims to protect the epoxy build coat from this. The post 90% RH exposure images (Figs 5.59, 5.60) show damage to the topcoat caused by slight movements of samples within reaction vessels during oxygen measurements. Susceptibility to impact damage due to embrittlement of the polyurethane coating is a well-known drawback (various heritage ironworkers, *pers. comm.*). If ironwork coated with a similar system is to be transported after coating, it is expected to require retouching of the polyurethane before assembly to repair impact damage to the topcoat (P. Meehan 2015, *pers. comm*).

Figure 6.11 *Failure of system similar to System A within 12 months of reinstatement in coastal environment. Corrosion staining evident on pale coloured topcoat.*

Iron responds dimensionally to thermal changes, expanding with increasing temperature and contracting with decreasing temperature. Epoxy resins cure by reaction creating cross linking between the resin and hardener (Carraher 2011, 128). This forms a rigid three dimensional structure with little dimensional response to changing temperature. Consequently, epoxy resin coatings on iron and steel are known to crack, particularly at joints where thermal expansion and contraction effects are greatest (Raedel and Buecker 2014; heritage ironwork practitioners *pers. comm.*). Cracks in coatings allow ingress of water and pollutants and become sites for corrosion of substrate metal. This may then cause the unsightly staining.

The high gloss of System B is its most notable feature although this may dull over time with exposure to an exterior environment with weathering and abrasion effects. The morphology of the iron surface can be seen, possibly due to the relatively low build of the primer coating (Fig. 5.39). Oil based coatings are more mobile than epoxy resins to accommodate the dimensional changes of metallic substrates more readily (Horovitz 1986). This minimises likelihood of cracking. Coating C has a low build and allows the substrate morphology to be seen readily. This may be an advantage as it is unlikely to obscure detail or may be undesirable in revealing the extent of pitting on a surface. The satin finish conforms to a historic aesthetic which may be a priority.

6.2.10 **Practicalities**

Much of the success of protective coatings relates to the quality of its application. Assuming no carelessness, the more challenging the application procedure the more likely are problems with the finished coating. System A requires the application of two coats of three two-pack coatings. Two-pack coatings involve mixing both parts of the coating in the correct ratio either by mass or volume to deliver optimum properties of the coating. Too little hardener and the coating will not cure fully, too much and the excess will remain as a sticky residue on the surface (Fig. 6.12).

***Figure 6.12** Showing an example of the effects of preparing two-pack coating in incorrect ratio of resin and hardener.*

Properties of the coatings change during application as reaction curing begins in the pot. Viscosity may be very low initially resulting in low build and run back from edges but gradually increases during application until it becomes stringy, bulky and difficult to attain a smooth finish with. The point at which the coating becomes too viscous and no longer produces a satisfactory finish must be judged. Non-uniform application across the structure or object may lead to more successful performance in some areas than in others. The rate of change in properties relates to cure time which in turn relies on environmental conditions (Leighs 2008a,b). Elevated temperatures accelerate curing and lower temperatures retard it. Additionally, two-part mixing can be wasteful of materials since without extensive experience it is difficult to predict the volumes required.

System B topcoat was notable for its long drying time and persistent tackiness. Were ironwork to be coated off site, based on this experience it would be at least two weeks before the object could be handled and transported without damaging the coating. Were the coating applied on site, particulate pickup and damage from passers-by, animals and so on would negatively impact on coating appearance and continuity. The slow drying time is likely responsible for extensive run-back from peaks (Figs 5.41, 5.42) and consequent low DFT in these areas.

6.2.11 Recommendations and endorsements

System B and Coating C are manufactured by a household name brand. This may be seen as an endorsement or a negative depending upon the perception of the decision maker. The product range manufactured by the brand suggests preparation of different formulations to meet the needs of particular situations (e.g. galvanised and high temperature surfaces) which may inspire confidence. Anecdotal evidence for and against use of these products can be found on many DIY and automotive websites and discussion forums. Although unlikely to offer balanced and insightful discussion in all cases, they may present useful experience of the difficulty or ease of use of the products by non-specialists and reports of successes or failures over time. Perhaps a subjective review of such feedback would offer a useful starting point for choosing coatings.

The manufacturer of System A is not a household name but is well known within engineering and coating sectors. Their products are used extensively in aggressive marine environments and for high profile projects such as the heavily publicised coating of the Forth Rail Bridge (Sherwin-Williams 2013) which ended the previous continuous painting cycle. The manufacturer advertises its credentials with an endorsements section on the product datasheets (Leighs 2008 a, b, c) including from large, private companies and national bodies and compliance with British Standards. Within heritage, coatings produced by this manufacturer have been used for small and large projects (Watkinson et al. 2005; Peter Meehan *pers. comm.*; Eura Conservation *pers. comm.*) with a consequent word-of-mouth effect which has likely increased their use. A non-specialist, for example the manager of a historic property with no conservation experience, may not have heard of this manufacturer and is unlikely to come across it without online research.

6.2.12 **Lifetime to maintenance and durability**

It is clear from manufacturer data sheets and British Standards that there is no guaranteed lifetime of a coating (British Standards Institute 2007; Leighs 2008 a, b, c). It is easy to see why. With so many variables (environment, corrodibility of substrate material, thoroughness of surface preparation, quality of coating application, adherence to stated over-coating intervals, DFT, holidays and more) it is impossible to guarantee the lifetime unless the substrate and the application are perfectly controlled. Figure 6.11 shows failure within 12 months of a coating system almost identical to System A applied by non-specialists over a substrate which was likely not desalinated thoroughly before coating and reassembly in its coastal environment (C4 or C5-M atmospheric corrosivity category). According to BS EN ISO 12944-5:1998 this system in a C4 environment should have had a High durability with first major maintenance after 15 years or more (British Standards Institute 1998). In a C5-M environment (aggressive coastal) the expected durability would be 5-15 years. The coating failed long before the predicted time.

The expected durability (time to first major maintenance) of System A is 15 years or more in an urban/industrial environment. A lifetime of 8 years is advertised by the manufacturer of Coating C. Lifetime of the primer for System B is not stated although it is advertised as ‘Long Lasting’ and no lifetime is given for the topcoat. According to BS EN ISO 12944-5:1998 (British Standards Institute 1998) the expected durability for such a system in an urban/industrial environment would be less than 5 years.

These predictions do not offer a helpful guide for scheduling maintenance. If a system is expected to require maintenance within five years, should this be scheduled at one year or four? The answer to this must be greater resolution of timescales through wider testing of substrates and environments on the part of the manufacturer or Standards Institute and ongoing vigilance and inspection of coated ironwork at intervals of a few months. Truly effective management of heritage preservation cannot occur with the level of uncertainty presented by the current standards.

On the basis of advertised lifetimes and predictions from British Standards, it would appear that System A offers the greatest lifetime to maintenance, followed by Coating C and System B. This cannot be inferred from short term, static RH testing carried out here with no concession to weathering processes or pollutants. Long term testing with cycling conditions of RH and temperature and introduction of corrosion promoting species consistent with atmospheric pollutants could offer this understanding of performance. British Standards and manufacturer predictions are based on accelerated testing. Proposed here is a programme of *real-time* testing on historic material which is time consuming and labour intensive but essential for the heritage sector to build the necessary evidence base for effective practice. The prospect of developing such a programme is discussed in 6.2.16 and 6.3.

6.2.13 **Corrosion prevention**

Oxygen consumption reported in 5.2.4, Figs 5.49-5.58 and Tables 5.10 and 5.11 indicates no corrosion of System A and Coating C iron samples as the consumption of the coated samples does not exceed that of the control coating samples. Small amounts of oxygen consumption may relate to discrepancies in surface area of coating applied which was difficult to standardise due to pitting of the sample surfaces. There is a significant difference (Table 5.12) between the corrosion rates of the uncoated substrate material and System A and Coating C samples underlining the significant corrosion reduction by the coating.

Oxygen consumption by the wrought iron samples was greater than by the coating controls for System B. It is assumed that this oxygen was consumed by corrosion reactions. Figure 5.57 shows a distinction between corrosion rate of System B coated samples and the Sa2.5 blasted samples which represent their uncoated substrates. System B does reduce the corrosion rate of the substrate but not as successfully as System A.

Based on predicted durability from the British Standards, alkyd coatings are not expected to perform as well as epoxy resin coatings so results for Systems A and B are not surprising. BS EN ISO 12944-5:1998 states that the same alkyd system has greater durability when applied to Sa2.5 blasted substrates than those retaining oxides (British Standards Institute 1998) so System B and Coating C results might be considered surprising. As the coatings themselves are not directly comparable, no conclusion can be drawn on this but the retained oxides of Coating C samples may be protective. It would be desirable to repeat the test with System B applied over a wire brushed substrate. This preparation method is advocated for this system but it is also recommended for use on bare steel surfaces hence testing on a blasted surface here. Much lower adhesion values with cohesion of oxides the failure point for Coating C suggests an element of caution is required when advocating coating application to corrosion products. This must be investigated further before firm conclusions are drawn. The very nature of oxide coatings varies greatly. The oxides here were fairly coherent and compact, in other contexts they may be lamellar and flaking (Figs 2.9, 2.11).

These results only relate to the conditions to which these samples were exposed, a high static RH with no wetting/drying cycles, atmospheric pollutants, wind, rain or ultraviolet radiation. Coating performance beyond this limited environment and time frame cannot be predicted from the results of this study.

6.2.14 Sample material

The challenge of assessing heritage conservation methods experimentally lies in the nature of the sample material and the method of quantification adopted. The individual nature of heritage metals whose corrosion layers have developed over many years, often in unknown and variable environmental conditions, means that the production of analogues to represent them in experimental study can be challenging if results are expected to reflect the reality of treating heritage objects.

There are specific contexts in which attempts to deliver standardised analogues that represent heritage objects are useful for reasons of reproducibility. Degrigny (2010) offers a clear methodology for generating standardised chloride-containing corrosion layers on copper alloys and iron on which to test the performance of protective coatings for corroded heritage metals. This worked effectively for producing comparative data between partners in the PROMET project (Argyropoulos et al. 2007). Nevertheless, there is inevitably a compromise in this approach between the imperfect representations of naturally generated corrosion layers and those grown in accelerated corrosion contexts, although this must be balanced against good reproducibility of analogue samples and the positive impact of this on data quality. Uniformity provided by analogues offers potential for ranking that can be fed back to real life scenarios by extrapolation using the context of ‘expected performance’.

The data revealed that it is possible to use the wrought iron railing to produce comparative test samples for determining the effect of selected surface cleaning techniques on the corrosion rate of historical iron. The corrosion rate of the samples was sufficiently consistent to allow comparison between surface treatments that would not be influenced by the nature of the sample. The graph of five uncleaned railing samples shows a good agreement between the oxygen consumption rates of the samples, demonstrated by the clustering of the points over the first 70 days (Fig. 5.15). Rate agreement between uncleaned samples 1 and 2 means their points on the graph overlie each other throughout the test period. The oxygen consumption rates do not form straight lines and to increase clarity no trendlines are shown. The trendline gradient for each sample over the first 75 days is given in Table 6.3. The slight falling off of the rate seen for each sample may be due to the limiting effect of diminishing oxygen concentration within the reaction vessels or a consequence of a build-up of newly formed corrosion products. It may also be that full adsorption of water into capillaries (see 2.3.1) reduces the rate of oxygen diffusion to the anodes on the metal surface.

Sample No.	Gradient
1	0.2246
2	0.2049
3	0.1866
4	0.2378
5	0.1702

Table 6.3 *Showing trendline gradients for first 75 days of oxygen consumption testing at 90% RH for uncleaned railing sample material.*

It is surprising that iron retaining vestiges of paint in a random survival pattern should show good agreement of corrosion rate for samples of similar nominal surface area. Minor differences in sample mass appear to have no influence on corrosion. Overall, the homogeneity of the slag distribution (see 5.1.1) likely provides for even corrosion patterns over the metal surface more akin to general corrosion than extensive localised pitting. The actual surface area of the samples clearly differs from calculations related to sample dimensions as surfaces are uneven and pocked and it may be this, rather than the mass of the samples, that creates differences in corrosion rate. This point is reinforced when the data for the railing and gasometer samples are considered (Table 6.4).

The railing and gasometer samples differ in extent of corrosion product and vestiges of existing corrosion products. As such, the only samples permitting direct comparison between sample materials are those aluminium oxide blasted to Sa2.5. Given the fall off in oxygen consumption rate over time evident with both sample materials, comparison is made by truncating the gasometer data (to 351 days) to match approximately the number of days oxygen consumption at 90% RH recorded for the railing material (338).

	Statistic	**Railing**	**Gasometer**
O_2 consumed *(mol/mm^2/year x 10^{-8})*	*Mean*	15.58	9.29
	Median	15.14	9.82
	Range	18.90	5.99
	Interquartile Range	11.64	1.61
	Standard Deviation	7.01	1.77
Fe converted *(mol/mm^2/year x 10^{-8})*	*Mean*	20.77	12.38
	Median	20.18	13.09
	Range	25.20	8.00
	Interquartile Range	15.20	2.16
	Standard Deviation	9.34	2.36

Table 6.4 *Descriptive statistics for railing and gasometer sample material blasted to Sa2.5 and exposed to 90%RH for 338 and 351 days respectively.*

The skewness values demonstrate that the data is not normally distributed therefore median and interquartile range are more appropriate measures of central tendency than mean and standard deviation. The median values for the railing wrought iron are higher than for the gasometer material signifying a greater corrosion rate. This is not unexpected given that the extent of corrosion on the railing prior to sampling was much greater than that on the gasometer despite both having been exposed to outdoor atmospheric corrosion over hundreds of years. The railing wrought iron has a greater slag content (Figs 5.1, 5.29) which may contribute to its higher corrosion rate. The range and interquartile range of the data sets indicate extent of sample standardisation. These values for the gasometer are smaller than for the railing suggesting greater standardisation and reproducibility. Again, this is not unexpected and is likely due to more extensive pitting of the railing material which leads to greater differences in surface area available for reaction between the samples.

Although it is difficult to draw conclusions from small sample populations, results indicate that standardisation of historic sample material is possible. It is nearly impossible to generate perfectly standardised, analogous samples with corrosion products accurately replicating those formed over many years of atmospheric corrosion and subject to the same corrosion mechanisms as historic wrought iron. It would seem from these results that historic sample material can be standardised sufficiently when care is taken to minimise chances of compositional differences, variation in surface area and extent of contamination with corrosive pollutants.

While standardisation of analogues is possible, transferring results to heritage contexts is difficult. The reality is that datasets can only ever be related to the test sample context. Extrapolating interpretation and contextualisation will always be necessary.

6.2.15 **Standards for corrosion protection by protective coatings**

6.2.15.1 *Existing standards and application to historic contexts*

The question of how suitable British Standards for coating ferrous metals are for application to heritage sector treatments must be considered. BS 5493:1977 *Code of practice for: Protective coating of iron and steel structures against corrosion* (British Standards Institute 1977) has been partially superseded by BS EN ISO 12944:1998 *Paints and varnishes – Corrosion protection of steel structures by protective paint systems* (British Standards Institute 1998). Both are considered here.

Employing these standards when devising coating strategies for historic wrought iron is problematic. The standards apply to modern steels which themselves conform to further British Standards of production and composition. Historic wrought iron might have been produced at any point over a one thousand years plus time span, is unlikely to have been standardised in its production and will exhibit a range of compositions (see 1.1). The standards BS 5493 and BS EN ISO 12944 assume that the paint specification is prepared prior to erection of a structure. Coating application is expected to be on new milled steel with corrosion products limited to mill scale formed during hot rolling and flash rusting from less than ideal storage conditions. This is not the case with historic wrought iron. Corrosion product layers built up over centuries may have caused extensive pitting of surfaces and may include deep seated corrosion-driving chlorides which are difficult to remove from pits and deep laminations. Structural members may have suffered loss of section through corrosion which prohibits blasting to deliver the expected level of surface preparation.

BS EN ISO 12944-3:1998 deals with measures to effectively design out of the structure any elements which make corrosion more likely or coating of surfaces difficult to achieve (British Standards Institute 1998). Access for maintenance work is planned at the design stage and any element inaccessible after construction is to be sufficiently protected to survive the expected lifetime of the structure without maintenance. The anticipated functional nature of the structures is underlined by the instruction that designs should be simple, avoiding complexity and shapes which promote corrosion. With historic ironwork the design of the structure is predetermined, likely to be decorative and convoluted and its expected lifetime would be survival in perpetuity according to conservation professional standards and ethics.

Descriptions of maintenance procedures are the closest that these standards come to conservation treatments in the first instance. Crucially, the standards expect maintenance to have been built into the initial design of an iron or steel structure. It is assumed that corrosion prevention measures have been maximised in the initial construction phase, that parts of a structure can be replaced, that structures have limited lifetimes and that facilitating maintenance was part of the original design. Re-blasting a structure to bare metal enabling full recoating is expected to be acceptable and feasible practice. Loss of original material, provided sufficient section remains to ensure structural stability, is not a concern.

Methods for testing coating properties are difficult to apply to and interpret for heritage materials. The drawbacks of nominal dry film thickness values are discussed in 6.2.7. Adhesion testing using pneumatic pull-off dollies is a standard test procedure for characterising coating properties and performance outlined in BS EN ISO 4624:2003 (British Standards Institute 2003). Standardisation requirements are that the coating be applied to uniform thickness on steel panels of uniform surface texture. The test is necessarily destructive as it assesses the failure point and mode of the coating adhesion to the substrate surface. Problems for the heritage sector in conducting this test arise from unevenly corroded and pitted surfaces which limit stability of the dollies during adhesion and prevent even coating application with pooling in pits and run back from peaks. A wider range of results is likely on inhomogeneous historic wrought iron surfaces which presents challenges for interpretation and raises questions over relevance of data.

Without doubt, British Standards can be useful to heritage ironwork practitioners despite the engineering/industrial focus that limits their relevance for and application to historic material in heritage contexts. However, it is critical to recognise their limitations and practitioners wishing to conform and offer an evidence base for their protocols and decision-making may not do this. Standardised and evidence based approaches are crucial to effective conservation practice. Practitioner flame cleaning highlighted variation between individual methods which are based on anecdotal evidence in the main and relate strongly to extent of training in conservation ethics. There is a wealth of experience of surface preparation and coating of historic wrought iron dispersed throughout the heritage ironwork practitioner community but these are individuals who do not publish widely and the benefit of this experience is not felt across conservation. Similarly, unless a blacksmith undertakes training in conservation he/she is unlikely to consider all facets of conservation ethics and operate with attention to concepts of original surface and appreciation of the line between conservation and restoration. The treatment of historic wrought iron is a cross-over discipline in this respect. Ethical principles apply but structures must often function safely which necessitates more extensive repair and replacement than might otherwise be ethical. The lack of linkage between anecdotal and quantitative evidence leads to uninformed decision-making and practice, dissatisfaction from those contracting work and ultimately, the concept that heritage is badly managed.

6.2.16 Heritage coating standards

The difficulties inherent in applying the existing British Standards directly to historic material have been discussed. The ideal would perhaps be to generate evidence based heritage standards to guide practice but this is not without challenges. The Drafting Committee list for the 1977 BS 5493 (British Standards Committee 1977) has approximately 50 names of individuals from public and private institutions who contributed to its content. The extent of this list and the sum total of knowledge and experience allows the document to cover a wide range of materials and processes in sufficient depth. It could be argued that given the variation in historic wrought iron and the vast array of structures and objects produced over time and still in existence, as much or more input would be needed from experts in the heritage sector to draw up fit-for-purpose guidelines. Producing an empirical evidence base for the standards would require an immense amount of research from the few heritage scientists working in this area. Testing a coating is not a simple process as the many permutations of a system (surface preparation level, number of coatings, number of coats of each coating and so on) must all be tested individually to produce guidance approaching the level of detail found in BS 5493:1977 or BS EN ISO 12944:1998 (British Standards Institute 1998). Development of a standardised method for testing would be essential for comparative data. Added to this is the requirement to update standards regularly with results of tests on the new coatings produced at a bewildering rate by manufacturers and all claiming to be the new wonder coating. If empirical-evidence based standards were required, the input of time and money would be unsupportable in such a small and poorly funded sector.

If clear limitations are accepted, there is perhaps scope for a set of standards offering a synergy of empirical evidence generated in laboratory contexts and anecdotal experience of successes, failures and practical and ethical considerations. This data could be built over time by as many individuals as are willing to contribute and in an ideal world this would lead to a culture of sharing experiences to improve practice for all. In this era of social media and instant communication this could be achieved readily with some coordination. Evidence may be in the form of treatment records and site photos showing modes of failure of coating systems or evidencing successes. Many practitioners make periodic return visits to site and managers of properties with treated ironwork could be encouraged to contribute. The commercial sensitivity of the data could be mitigated by careful moderation of the contributions.

A major benefit of this semi-anecdotal approach to data gathering would be the ability to survey coatings over many years. This move away from the accelerated testing advocated in industrial and engineering contexts may offer better resolution of data regarding times and modes of failure of coatings which could inform coating selection and maintenance scheduling. Clear criteria would underpin assessment of application and short and long term performance. BS EN ISO 12944:1998 currently offers categories of ‘low’ 2-5 years, ‘medium’ 5-15 years and ‘high’ more than 15 years for protective coating performance in a given environment (British Standards Institute 1998). Evidence from practitioners and managers could narrow these categories or, alternatively, suggest that coatings do not fit neatly into these categories and evidence the need for further investigation of failures. It would require the input of environmental data.

Although it may not be possible to provide empirical evidence for the performance of every coating type from each manufacturer, it would be possible to draw information from a range of researchers investigating mechanisms of wrought iron corrosion. For example, there is a trade-off between optimal performance of coatings on an Sa2.5 blasted surface and the possible reduction of corrosion rate through retention of the coherent oxide layer present on historic iron objects which have been subject to centuries of atmospheric corrosion. If the mechanisms of protection were more clearly understood, it might be possible for practitioners to characterise and retain protective oxides and limit surface preparation to wire brushing and perhaps rubbing with emery paper to improve keying and adhesion of coatings. This would satisfy the need to reduce corrosion rates whilst conforming to conservation ethics. This study has begun the cost benefit analysis of surface tolerant coatings relative to greater surface preparation but more work is required to assess long term protection.

6.3 Standardising test methods for heritage: scope, limitations and further work

6.3.1 Scope of method for heritage sector studies

This study aimed to develop fit-for-purpose test methods for treatment of historic wrought iron. The results support the methods employed here to standardise surface preparation and application of protective coatings, the use of appropriate control samples and the generation of quantitative corrosion rate data via oxygen consumption measurements. The ability to standardise historic wrought iron samples was demonstrated, encouraging its use in other studies. The method can be applied readily to wrought iron of all periods but also to cast iron and mild steel sample material and to investigating the range of variables required to underpin predictive guidelines for practitioners.

Coated and uncoated samples show good agreement of results for samples treated in the same manner (Figs 5.10-5.15, 5.49-5.51). This implies a good level of standardisation and reproducibility even with samples of historic wrought iron. The protocol for running sufficient numbers of appropriate control samples to determine their oxygen consumption should allow corrosion rates and treatment effects to be compared across results from workers using different sample materials. A database of corrosion rates of untreated samples of wrought iron from different sources would be illuminating. Variability in corrosion rates of wrought iron of different periods and compositions would indicate the extent to which a one-size-fits-all approach to treatment of historic wrought iron is appropriate. This data will be generated as part of continuing work at Cardiff as more sample material is sourced. Other workers using the same method would be encouraged to pool their data on uncoated wrought iron for comparison alongside details of metallurgy.

Flame cleaning by practitioners demonstrated that supporting laboratory methods and results with samples prepared by practitioners using their preferred techniques allows verification of legitimacy of laboratory testing. This good practice could be extended in future to other techniques examined in this study. It would also permit close investigation of the diversity of practice and methods within the sector and impact of differing protocols on success or failure of treatments. This would feed directly into guidance for practitioners which would be entirely focused on and relevant to their practices. Extending this yet further to coating application, practitioner methods of spray coating could be compared to brush application of the same coating. The importance of this being carried out in the field or shop is that application methods must be fit-for-purpose for the situation in which they will be employed. The practicalities of using that method in the field are integral to its success. Laboratory testing does not allow challenging of the techniques to this extent.

Most standardised laboratory testing of protective coating systems for ferrous metals aims to determine whether the coatings have the properties in given environments which suggest that they will offer a satisfactory level of protection. Testing is normally accelerated by exposure of samples to more aggressive environments than would be expected. The properties of the coatings after these accelerated artificial-ageing exposures are examined and predicted performance extrapolated from the results.

The real-time method employed for examining coating performance here is not related to determination of properties after ageing but to measurement of corrosion rate of coated wrought iron substrates during exposure to a given environment, in this case a static high humidity. The difference between this and the approach outlined in the standard is that one level of extrapolation is removed by the measurement of corrosion rate from oxygen consumption. Running sufficient numbers of control samples gives a degree of confidence in measurement of the oxygen consumption of the coatings themselves and allows the determination of the oxygen consumption by the substrate material which is expected to be due to corrosion. This is therefore a direct measure of the protective performance of the coating in the test environment. Likewise, oxygen consumption of prepared, uncoated wrought iron allows corrosion rate in the test environment to be quantitatively measured.

6.3.2 Limitations and further work

Although successful, the methods developed here are not without their limitations. Laboratory preparation of samples permits a degree of control and attention to detail through small scale actions in a managed setting that is not achievable in the field or shop. Blasting samples using laboratory airbrasive units with glove boxes, tailored lighting and magnification to increase visibility of surfaces allows assessment of tightly controlled end points of cleaning which is not possible for practitioners. The blast media are more akin to fine powders than the grits commonly used for blasting structures in practice. Resultant surface profiles will therefore be coarser than those attained in this study which may have some impact on corrosion rate tested here but would likely be more noticeable as differences in adhesion and numbers of rogue peaks with low build coatings.

Correlation of the test environment to real-life conditions in exterior exposure of historic wrought iron is limited in this case, being static 90% RH at 20°C. This extreme of humidity is not unlikely in Britain (Met Office 2014) but static RH and temperature represents unreal conditions. There is no concession to the influence of pollutants, ultraviolet radiation, wetting and drying cycles, extremes of temperature and other factors in this study. The method of corrosion rate measurement relies on the samples being sealed in the reaction vessels for continuous periods of fairly long duration in the case of samples which are consuming oxygen slowly. It would degrade the quality of the data were the reaction vessels opened frequently to change the conditions inside, for example to cycle RH. The variable that can be altered readily within the climatic chambers is temperature. This could be programmed to reflect diurnal and seasonal changes. The effect of cycling temperature on the RH within the reaction vessels with silica gel must be examined. The extent to which conditioned silica gel will buffer the change in RH with temperature is not known. Addressing these limitations will be a focus for further work in this area building on the methods used in this study. Potential foci for continued research are outlined in Table 6.5.

	Variable	**Focus**
Corrosion rate measurement via oxygen consumption	*Relative Humidity*	Wet/dry cycles
	Ultra Violet Radiation	Coating breakdown
	Temperature	Diurnal and seasonal
	Coating Damage	Scribed samples
	Corrosion Accelerants	Chlorides/seawater
	Joints and Crevices	Coating performance

Table 6.5 *Further work test variables for corrosion rate investigations.*

A short term goal and integral to further work is dissemination of results and engagement with practitioners. This experimental investigation was developed to meet a sector need which was evident in communication with heritage ironwork practitioners and specifiers of treatment programmes for wrought iron and in the commissioning of this project by Historic Scotland. It is essential that results are fed back to the sector to justify investment of time and money in the project by individuals and organisations. It is only by reporting results that benefit can be felt by the sector and researchers can hope to influence practices and encourage evidence based management. Publication of results in heritage sector and corrosion journals will disseminate findings to a portion of the heritage community but it is unlikely that most practitioners have access to corrosion journals. The next step is the production of clear, freely accessible sector based guidance that links results to methods and balances corrosion rates and expected lifetimes to practicalities and costs.

7 Conclusions

7.1 Cost benefit

This study had as its aim to perform a cost benefit analysis of surface preparation methods and protective coatings for wrought iron. In reality, this is very complex equation. It is possible to enter empirical data of corrosion rates not as distinct values, given differences in substrate composition, corrosivity of environments and a range of other factors, but as comparatives. Compared to the uncleaned wrought iron, crushed walnut blasting and sodium hydroxide immersion reduce corrosion rates. Blasting to Sa 2.5 with aluminium oxide and glass beads increases corrosion rate. Flame cleaning greatly increases corrosion rate (approximately by a factor of 4). This may seem to imply that crushed walnut blasting or sodium hydroxide immersion should be the surface preparation methods of choice yet, practically, immersion in chemical solutions relies on being able to disassemble a structure and neither produce surfaces with keying for adhesion of coatings.

This introduces another complication. Surface preparation is a precursor to coating. Whilst corrosion rates of uncoated substrates might indicate relative risk to the underlying metal if coatings are damaged, surface preparation must also aim to maximise performance of the protective coatings. Methods retaining oxides (for example, the crushed walnut and sodium hydroxide techniques which performed well in uncoated testing) do not comply with recommendations for surface preparation prior to coating with two-pack epoxy resin coatings or indeed most non-surface-tolerant coatings. Coating performance may be compromised with these techniques. They do, however, comply with conservation ethics. A major factor on the ‘cost’ side of the equation is loss of original material associated with surface preparation to Sa2.5. Aluminium oxide and glass beads blasting applied to Sa2.5 level may remove corrosion products and contaminants which potentially undermine coating performance but they also remove original material and associated evidence.

Cost benefit analysis of coatings is subject to similar challenges. What can be said with confidence is that there is no benefit to applying System B over a substrate surface blasted to Sa2.5. Reduction of corrosion rate of the uncoated Sa2.5 substrate is much less than with the epoxy resin System A and loss of original material is extensive as compared with Coating C. System A and Coating C offer the benefit of a reduction in corrosion rate of Sa2.5 blasted and wire brushed substrates respectively. With System A, this is countered by the cost of loss of original material, practical difficulties of coating application, financial implications of necessary contractors and maintenance regimes requiring full re-blasting and re-coating. Coating C has the benefits of reducing corrosion rates, conforming to ethics of retention of original material, simple maintenance regimes and low financial cost. The drawbacks are the unknown long term implications of retention of oxides on performance of the coating. Low adhesion values of oxides to substrate are a concern.

Despite difficulties in performing true cost benefit analysis of the surface preparations and coatings tested here, there are clear indications that this will be possible with a larger dataset gathered over longer timescales. It also requires input of specifics for each project such as budget, availability of expertise, required lifetimes to maintenance, importance of historic aesthetic and so forth. A very welcome outcome of this study is the suggestion that there is potentially a successful surface preparation and alkyd coating combination for low budget, minimal intervention projects (Coating C) which conforms to ethical and aesthetic requirements and performs as well (in relatively short term testing at static high RH) as the highly interventive, higher cost option of blasting and applying an epoxy resin system (System A). This horses-for-courses approach appears to offer options to suit a range of treatment contexts and specifier priorities.

7.2 Method

This study has developed a protocol which allows an oxygen consumption method previously used on uncoated archaeological objects to be employed as proxy corrosion rate measurement for coated iron samples. Consumption of oxygen can be accounted for by this method through measurement of control samples. The same method can be applied to coated and uncoated samples and by other workers and standardised by use of controls. A method for processing the data of the oxygen consumption measurements is also proposed which can be applied to work out the number of moles of iron converted for the oxygen consumed assuming the predominant reaction is the formation of FeOOH. This can again be utilised (with caveats) by other workers to build a database of complementary results which would generate a rich resource for theoretical study and practical application of treatments for historic wrought iron heritage.

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9 Appendices

9.1 Appendix 1: Recommended surface preparation methods

Table of recommendations of surface preparation techniques in heritage sector publications after: Wilson et al. 2008, 5; Childs 1985, 27; Ashurst and Ashurst 1988; Godfraind et al. 2012

Nb: Test on cast iron but results likely useful when considering wrought iron surface preparation.

Nb: Aim to retain closely adherent oxide layers influences perceived advantages/disadvantages.

* Relates to sandblasting, the use of which is now prohibited in Britain and elsewhere

Cleaning method	**Description**	**Advantages**	**Disadvantages**	**Recommendations**
Manual & power tool cleaning	Chipping, scraping and brushing to remove surface coverings	Easy Inexpensive Wire brush less damaging to oxide layer than other manual and power tool methods Cheap Easy Safe Effective on light rust Simple techniques Useful as first stage in cleaning process Relatively good control and visibility with manual techniques	Slow Labour intensive Not completely effective at paint removal Rotary abrasive disc and needle gun (high pressure) led to fragmentation of oxide layer Only removes loose rust; burnishes underlying rust (wire brushing) Manual techniques ineffective Scoring of surface and loss of detail possible Difficult to reach some areas of structure Restrictions on use of vibrating tools (e.g. needlegun)	**Recommended** (wire brushing recommended in conjunction with other methods such as flame cleaning or blast cleaning with 'soft' blast media) **Recommended** if applied with care
Laser cleaning	Laser beam (532nm or 1064nm) blast paint from object surface. Technique designed for stone cleaning.	-----	Expensive Ineffective Impractical	**Not recommended**
Flame cleaning	Flame (oxyacetylene or oxypropane) passed over	Fast and effective Oxide layer well preserved	Must be carried out by a specialist	**Recommended**

	metal surface to remove corrosion products and loose mill scale. Remaining loose corrosion products can be removed by wire brushing	Fairly inexpensive Removes moisture Burns off part scale Effective removal of paint, mill scale and corrosion products Can apply in situ Considered particularly suitable for wrought iron as only loose mill scale and rust removed	Health & safety concerns – vaporisation of toxic paints Buckles thin metal Not very effective Slow on large structures Warping of thin sections Fire hazard	(use in conjunction with manual wire brushing preferred) (under controlled conditions) Thought to be more appropriate for wrought than cast iron
Aqueous washing methods	Includes cold-water pressure washing, warm water washing, high pressure steam	Aqueous methods are effective at removal of soluble salts High pressure steam removes oils, waxes and grease		
Chemical cleaning	Corrosion product and coating removal usually requiring immersion of the object in a chemical bath followed by thorough rinsing Can include the use of mild detergents and acid cleaners	No chemical ingress into metal microstructure noticed Phosphoric acid may have helped in retention of surface oxide layer Inexpensive – can be carried out by homeowner (dichloromethane) or specialist Effective Controllable Can leave inhibited surface	Dichloromethane may have damaged surface profile HCl and caustic soda completely removed oxide layer Health & safety concerns – proposed European Council ban on use of dichloromethane (now in force) Dangerous; needs thorough rinsing and drying Attacks tin and zinc coatings	**Not recommended** (proposed further research of phosphoric acid treatment)

		Phosphorus containing solutions can form protective oxides 2-4% phosphoric acid (pickling acid) useful for removal of heavy rust staining	Cannot be carried out *in situ* Bath dimensions dictate size of objects/ structures treated Dips only suitable for dismantled structures	
Blast cleaning ('hard' media – alumina, chilled iron, copper slag, olivine, garnet, glass grit, glass beads, Sponge Jet 30, Sponge Jet 120)	Airborne abrasive particles blast iron surface producing roughened and clean surface. Control: type and diameter of grit, blasting pressure, blasting distance, blasting time, angle between blasting nozzle and surface – these factors often dictated in practice by object/structure and blasting equipment.	Inexpensive Effective* No moisture* Fine abrasive removes some surface contaminants* Fast Effective Quickest and most effective method Resultant surface maximises coating adhesion Limited removal of contaminants	Increased strength noticed in 3-point bend test – possible decrease in toughness Danger of galvanic corrosion if metal blast medium used Blast media particles and other debris impacted into iron surface Oxide layer not retained Must be carried out by a specialist Expensive* Dusty* - must be removed before coating Unpleasant for operatives* Can lead to loss of detail on wrought iron Hazardous Aggressive Risk of damage to fine, decorative detail Poor visibility	**Not recommended** Generally considered appropriate for cast and wrought iron. **Not recommended** Softest abrasive and smallest particle size should be chosen

			Use limited to structural iron and steelwork Waste collection and disposal costly especially with lead coating detritus	
Blast cleaning ('soft' media - walnut, plastic, dry ice)	As above.	Fast Highly effective Oxide layer well preserved No increase in strength of substrate or impacted blast media Dry ice blasting leaves no residue	More expensive Must be carried out by a specialist	**Recommended** (under controlled conditions)
Wet blast cleaning (with glass grit)		Effective Removes soluble contaminants No dust Preferable to dry blasting where lead based paints are present Effective washing of iron chlorides and sulphates from corrosion pits Effective – less so than dry blasting but more controllable	Immediate post-cleaning corrosion Oxide layer generally not retained Must be carried out by a specialist Drying problems cause re-rusting Possible penetration of water at junctions Slow Poor visibility Run off can stain surrounding building material Disposal of resultant slurry difficult	-----

Nb: Test on cast iron but results likely useful when considering wrought iron surface preparation.

Nb: Aim to retain closely adherent oxide layers influences perceived advantages/disadvantages.

* Relates to sandblasting, the use of which is now prohibited in Britain and elsewhere

9.2 Appendix 2: Table of coating details

Details of coating chemistry, surface preparation requirements, application methods and curing and overcoating intervals.

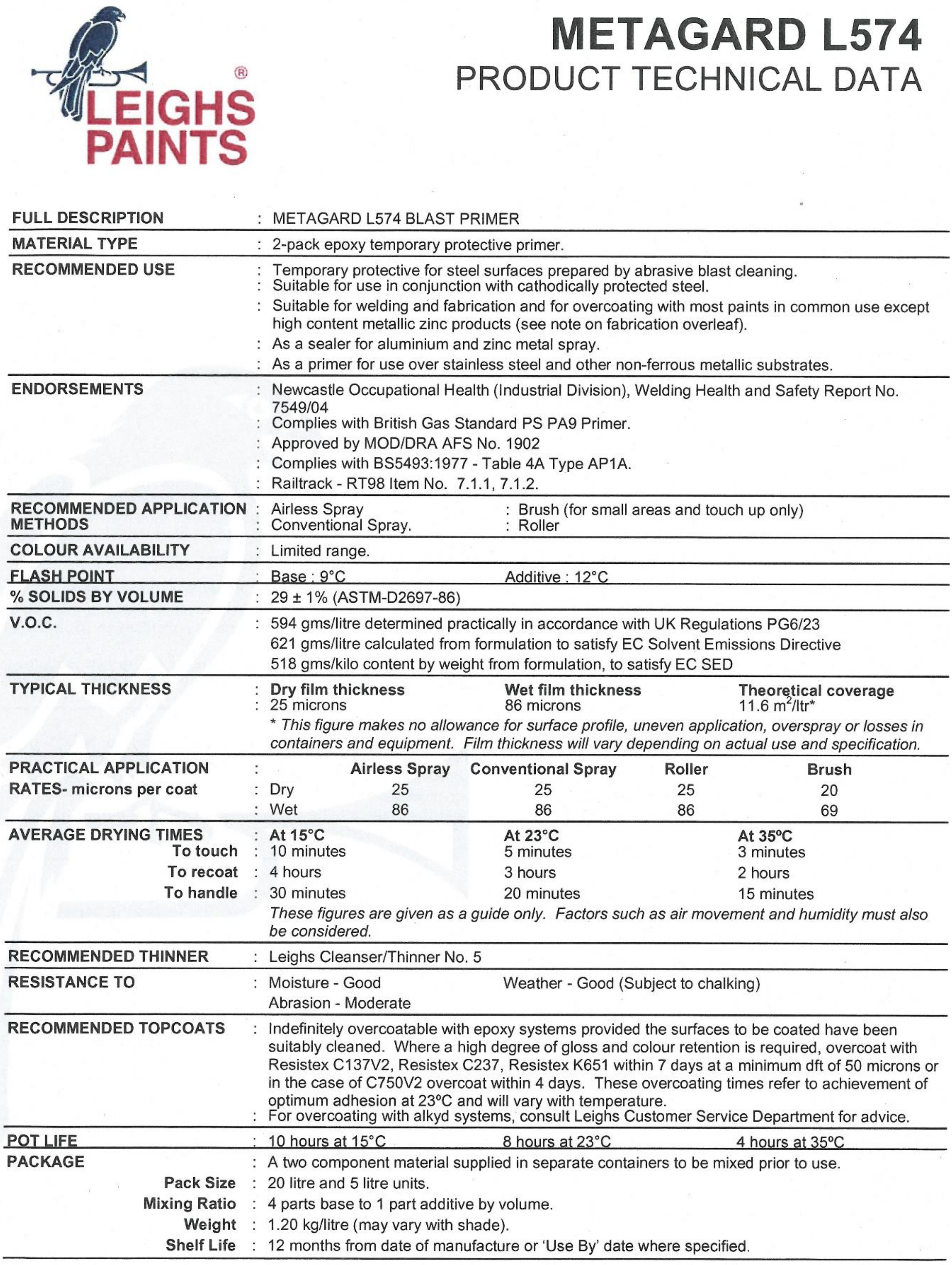
Manuf	***Coating***		***Chemistry***	***Surface Preparation***	***Application***	***Coats***	***Application Conditions***	***Overcoating Interval***
Leighs	Primer	Metagard L574	Two-pack epoxy	Sa2.5. Primer for blast cleaned substrates. Average surface profile in the range 30-50 microns.	Brush Roller Spray	DFT brush: 20µm/coat	Ambient 10^{o}C + Substrate 3^{o}C above dew point	Recoatable: **15°C 23°C 35°C** 4hrs 3hrs 2hrs
	Primer/ build	Epigrip C400V3	Two-pack epoxy – zinc rich	Sa2.5. Average surface profile in the range 50-75 microns. Ensure surfaces to be coated are clean, dry and free from all surface contamination. Manually prepared surfaces to min. St3. Application to such surfaces should be by brush or roller where the mechanical action will aid adhesion.	Brush Roller Spray	DFT brush: 65µm/coat	Ambient 10^{o}C + Substrate 3^{o}C above dew point RH≤90%	Recoatable: **15°C 23°C 35°C** 5 hrs 3½ hrs 2 hrs Resistex within 7 days.
	Topcoat	Resistex C137V2	Two-pack acrylic polyurethane	Ensure surfaces to be coated are clean, dry and free from all surface contamination.	Brush Roller Spray	DFT brush: 25-50 µm/coat*	Ambient 10^{o}C + Substrate 3^{o}C above dew point	Recoatable: **15°C 23°C 35°C** 8 hrs 6 hrs 4 hrs
Hammeri	Primer	Red Oxide Primer	Oil-based	Surfaces clean and dry. Remove loose rust, scale and paint with wire brush then rub down with coarse abrasive paper to provide firm surface. Abrade bare steel with coarse abrasive paper. Degrease all surfaces with Hammerite Brush Cleaner and Thinners and allow to dry.	Brush Roller	2		Min. 6 hours between coats. Topcoat best results after 24 hours.

	Primer	No. 1 Rust Beater	Oil-based	Remove loose rust, scale and paint by wire brushing or rubbing down with coarse abrasive paper. Abrade clean steel with emery paper to provide a key. Degrease where necessary with white spirit, rinse with clean water and allow to dry.	Brush	2	8-25°C	Touch dry 2 hours. Min. 6 hours between coats. Topcoat best results after 24 hours.
	Topcoat	Garage Door	Oil-based	Surface dry and free from loose rust and mill scale, paint, oil and grease. Lightly abrade painted surfaces with suitable abrasive paper. Wire brush to remove rust if necessary. Degrease where necessary with white spirit.	Brush	1 or 2	8-25°C	Touch dry 4 hours. Recoatable 16 hours.
	Single coat system	Direct to Rust Metal Paint	Oil-based	Abrade smooth surfaces and remove all loose rust and flaking paint with a wire brush. Remove dirt, dust and grease with diluted detergent. Rinse with clean water and allow time to dry.	Brush Spray	1 (prev. coated) or 2 (bare, rusty)	8-25°C Do not over apply – sagging.	Touch dry 1-2 hours. Recoatable 4 hours.

* The actual thickness within the quoted range will depend on many variables including ambient conditions, type of brush or roller used and operator expertise

9.3 Appendix 3: Leighs Metagard L574 product technical data

Leighs Metagard primer manufacturer datasheet.



LEIGHS PAINTS®

METAGARD L574
PRODUCT TECHNICAL DATA

FULL DESCRIPTION : METAGARD L574 BLAST PRIMER

MATERIAL TYPE : 2-pack epoxy temporary protective primer.

RECOMMENDED USE
: Temporary protective for steel surfaces prepared by abrasive blast cleaning.
: Suitable for use in conjunction with cathodically protected steel.
: Suitable for welding and fabrication and for overcoating with most paints in common use except high content metallic zinc products (see note on fabrication overleaf).
: As a sealer for aluminium and zinc metal spray.
: As a primer for use over stainless steel and other non-ferrous metallic substrates.

ENDORSEMENTS
: Newcastle Occupational Health (Industrial Division), Welding Health and Safety Report No. 7549/04
: Complies with British Gas Standard PS PA9 Primer.
: Approved by MOD/DRA AFS No. 1902
: Complies with BS5493:1977 - Table 4A Type AP1A.
: Railtrack - RT98 Item No. 7.1.1, 7.1.2.

RECOMMENDED APPLICATION METHODS
: Airless Spray : Brush (for small areas and touch up only)
: Conventional Spray. : Roller

COLOUR AVAILABILITY : Limited range.

FLASH POINT : Base : 9°C Additive : 12°C

% SOLIDS BY VOLUME : 29 ± 1% (ASTM-D2697-86)

V.O.C.
: 594 gms/litre determined practically in accordance with UK Regulations PG6/23
621 gms/litre calculated from formulation to satisfy EC Solvent Emissions Directive
518 gms/kilo content by weight from formulation, to satisfy EC SED

TYPICAL THICKNESS

Dry film thickness	Wet film thickness	Theoretical coverage
25 microns	86 microns	11.6 m^2/ltr*

** This figure makes no allowance for surface profile, uneven application, overspray or losses in containers and equipment. Film thickness will vary depending on actual use and specification.*

PRACTICAL APPLICATION RATES- microns per coat

	Airless Spray	Conventional Spray	Roller	Brush
Dry	25	25	25	20
Wet	86	86	86	69

AVERAGE DRYING TIMES

	At 15°C	At 23°C	At 35°C
To touch	10 minutes	5 minutes	3 minutes
To recoat	4 hours	3 hours	2 hours
To handle	30 minutes	20 minutes	15 minutes

These figures are given as a guide only. Factors such as air movement and humidity must also be considered.

RECOMMENDED THINNER : Leighs Cleanser/Thinner No. 5

RESISTANCE TO : Moisture - Good Weather - Good (Subject to chalking)
Abrasion - Moderate

RECOMMENDED TOPCOATS
: Indefinitely overcoatable with epoxy systems provided the surfaces to be coated have been suitably cleaned. Where a high degree of gloss and colour retention is required, overcoat with Resistex C137V2, Resistex C237, Resistex K651 within 7 days at a minimum dft of 50 microns or in the case of C750V2 overcoat within 4 days. These overcoating times refer to achievement of optimum adhesion at 23°C and will vary with temperature.
: For overcoating with alkyd systems, consult Leighs Customer Service Department for advice.

POT LIFE : 10 hours at 15°C 8 hours at 23°C 4 hours at 35°C

PACKAGE : A two component material supplied in separate containers to be mixed prior to use.
Pack Size : 20 litre and 5 litre units.
Mixing Ratio : 4 parts base to 1 part additive by volume.
Weight : 1.20 kg/litre (may vary with shade).
Shelf Life : 12 months from date of manufacture or 'Use By' date where specified.

SURFACE PREPARATION:

FERROUS SURFACES: For optimum performance use round steel shot and blast clean to Sa2½ BS7079:Part A1:1989 (ISO 8501-1:1988). Average surface profile in the range 30-50 microns.

NON FERROUS SURFACES: For optimum adhesion all surfaces should be flash blasted using non-metallic abrasive and coated with L574 within 4 hours of blasting. Under conditions of high humidity a shorter period will be necessary.

ALL SURFACES: Ensure surfaces to be coated are clean, dry and free from all surface contamination..

APPLICATION EQUIPMENT:

Airless Spray

Nozzle Size	:	0.38mm (15 thou)
Fan Angle	:	80°
Operating Pressure	:	155kg/cm² (2200 psi)

The airless spray details given above are intended as a guide only. Details such as fluid hose length and diameter, paint temperature and job shape and size all have an effect on the spray tip and operating pressure chosen. However, the operating pressure should be the lowest possible consistent with satisfactory atomisation. As conditions will vary from job to job, it is the applicators' responsibility to ensure that the equipment in use has been set up to give the best results. If in doubt Leighs Customer Service Department should be consulted.

Conventional Spray

Nozzle Size	:	1.27mm (50 thou)
Atomising Pressure	:	3.5kg/cm² (50 psi)
Fluid Pressure	:	1.0kg/cm² (15 psi)

The details of atomising pressure, fluid pressure and nozzle size are given as a guide. It may be found that slight variations of pressure will provide optimum atomisation in some circumstances according to the set up in use. Atomising air pressure depends on the air cap in use and the fluid pressure depends on the length of line and direction of feed i.e. horizontal or vertical.

Brush The material is suitable for brush application to small areas and for touch up purposes.

Roller The material is suitable for roller application.

Preparation and Build Up: Metagard L574 is not intended to replace a coat of primer in the main paint specification, it is designed to provide temporary protection, until the specified paint scheme can be applied. However in practice the use of Metagard L574 does make a substantial contribution to the performance of the complete paint specification in terms of ultimate durability and resistance to corrosion.

The applied dry film thickness of prefabrication primers is normally below 30 microns. At this level of dry film thickness, factors such as blast profile, unevenness of application and severity of exposure conditions may significantly affect the performance.

APPLICATION CONDITIONS AND OVERCOATING:

Epoxy paints should preferably be applied at temperatures in excess of 10ºC. In conditions of high relative humidity, i.e. 80-85% good ventilation conditions are essential. Substrate temperature should be at least 3°C above the dew point and always above 0°C.

At application temperatures below 10°C, drying and curing times will be significantly extended, and spraying characteristics may be impaired. Application at ambient air temperatures below 5°C is not recommended.

In order to achieve optimum water and chemical resistance, temperature needs to be maintained above 10ºC during curing.

If it is desired to overcoat outside the times stated on the data sheet, please seek advice of Leighs Customer Service Department.

For full notes, see data sheet entitled 'Spreading Rates and Overcoating Times'.

ADDITIONAL NOTES:

Drying times, curing times and pot life should be considered as a guide only.

The curing reaction of epoxies commences immediately the two components are mixed, and since the reaction is dependent on temperature, the curing time and pot life will be approximately halved by a 10°C increase in temperature and doubled by a 10°C decrease in temperature.

Fabrication: While Metagard L574 Primer is classed and approved as a welding primer, under certain types of welding operations e.g. high speed twin-fillet welding, fabricators are advised to satisfy themselves that the product is suitable for their particular welding process.

Epoxy Coatings - Tropical Use: Epoxy paints at the time of mixing should not exceed a temperature of 35ºC. Use of these products outside of the pot life may result in inferior adhesion properties even if the materials appear fit for application. Thinning the mixed product will not alleviate this problem.

It is not advisable to apply epoxy coatings when the air and substrate temperatures exceed 45ºC. These conditions can introduce paint film formation defects, such as dry spray. bubbling and pinholing etc.

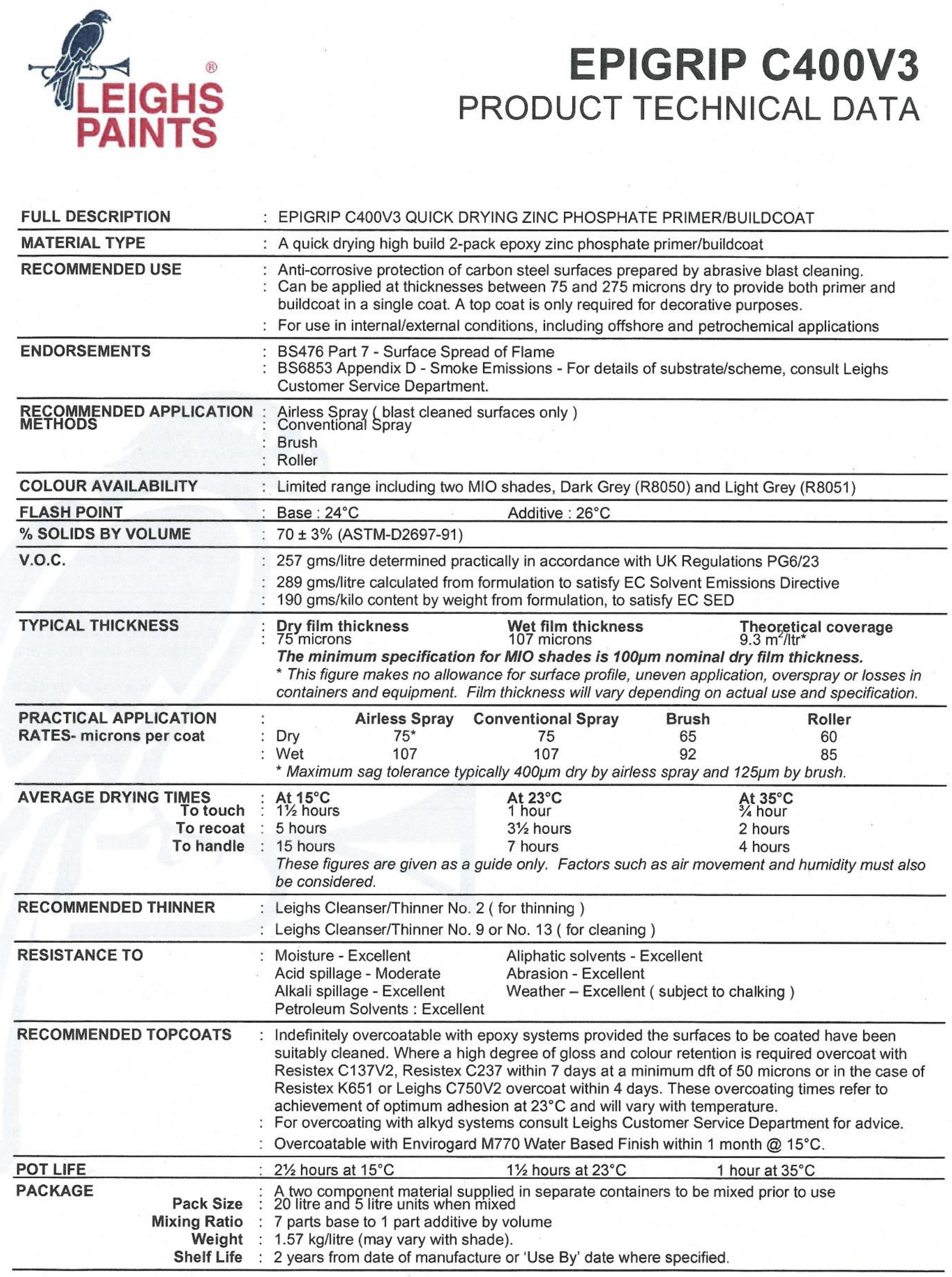
Numerical values quoted for physical data may vary slightly from batch to batch.

HEALTH AND SAFETY:

Consult Product Health and Safety Data Sheet for information on safe storage, handling and application of this product.

9.4 Appendix 4: Leighs Epigrip C400V3 product technical data

Leighs Epigrip build coat manufacturer datasheet.



LEIGHS PAINTS®

EPIGRIP C400V3
PRODUCT TECHNICAL DATA

FULL DESCRIPTION : EPIGRIP C400V3 QUICK DRYING ZINC PHOSPHATE PRIMER/BUILDCOAT

MATERIAL TYPE : A quick drying high build 2-pack epoxy zinc phosphate primer/buildcoat

RECOMMENDED USE
: Anti-corrosive protection of carbon steel surfaces prepared by abrasive blast cleaning.
: Can be applied at thicknesses between 75 and 275 microns dry to provide both primer and buildcoat in a single coat. A top coat is only required for decorative purposes.
: For use in internal/external conditions, including offshore and petrochemical applications

ENDORSEMENTS
: BS476 Part 7 - Surface Spread of Flame
: BS6853 Appendix D - Smoke Emissions - For details of substrate/scheme, consult Leighs Customer Service Department.

RECOMMENDED APPLICATION METHODS
: Airless Spray (blast cleaned surfaces only)
: Conventional Spray
: Brush
: Roller

COLOUR AVAILABILITY : Limited range including two MIO shades, Dark Grey (R8050) and Light Grey (R8051)

FLASH POINT : Base : 24°C Additive : 26°C

% SOLIDS BY VOLUME : 70 ± 3% (ASTM-D2697-91)

V.O.C.
: 257 gms/litre determined practically in accordance with UK Regulations PG6/23
: 289 gms/litre calculated from formulation to satisfy EC Solvent Emissions Directive
: 190 gms/kilo content by weight from formulation, to satisfy EC SED

TYPICAL THICKNESS

Dry film thickness	Wet film thickness	Theoretical coverage
75 microns	107 microns	9.3 m²/ltr*

The minimum specification for MIO shades is 100µm nominal dry film thickness.

** This figure makes no allowance for surface profile, uneven application, overspray or losses in containers and equipment. Film thickness will vary depending on actual use and specification.*

PRACTICAL APPLICATION RATES- microns per coat

	Airless Spray	Conventional Spray	Brush	Roller
Dry	75*	75	65	60
Wet	107	107	92	85

** Maximum sag tolerance typically 400µm dry by airless spray and 125µm by brush.*

AVERAGE DRYING TIMES

	At 15°C	At 23°C	At 35°C
To touch	1½ hours	1 hour	¾ hour
To recoat	5 hours	3½ hours	2 hours
To handle	15 hours	7 hours	4 hours

These figures are given as a guide only. Factors such as air movement and humidity must also be considered.

RECOMMENDED THINNER
: Leighs Cleanser/Thinner No. 2 (for thinning)
: Leighs Cleanser/Thinner No. 9 or No. 13 (for cleaning)

RESISTANCE TO

Moisture - Excellent	Aliphatic solvents - Excellent
Acid spillage - Moderate	Abrasion - Excellent
Alkali spillage - Excellent	Weather – Excellent (subject to chalking)
Petroleum Solvents : Excellent	

RECOMMENDED TOPCOATS
: Indefinitely overcoatable with epoxy systems provided the surfaces to be coated have been suitably cleaned. Where a high degree of gloss and colour retention is required overcoat with Resistex C137V2, Resistex C237 within 7 days at a minimum dft of 50 microns or in the case of Resistex K651 or Leighs C750V2 overcoat within 4 days. These overcoating times refer to achievement of optimum adhesion at 23°C and will vary with temperature.
: For overcoating with alkyd systems consult Leighs Customer Service Department for advice.
: Overcoatable with Envirogard M770 Water Based Finish within 1 month @ 15°C.

POT LIFE : 2½ hours at 15°C 1½ hours at 23°C 1 hour at 35°C

PACKAGE : A two component material supplied in separate containers to be mixed prior to use
Pack Size : 20 litre and 5 litre units when mixed
Mixing Ratio : 7 parts base to 1 part additive by volume
Weight : 1.57 kg/litre (may vary with shade).
Shelf Life : 2 years from date of manufacture or ‘Use By’ date where specified.

SURFACE PREPARATION:

Blast clean to Sa.2½ BS EN ISO 8501-1:2001. Average surface profile in the range 50-75 microns.
Ensure surfaces to be coated are clean, dry and free from all surface contamination.
Manually prepared surfaces should be prepared to a minimum standard of ST.3 BS EN ISO 8501-1:2001 at the time of coating.
Application to such surfaces should be by brush or roller where the mechanical action will aid adhesion.

APPLICATION EQUIPMENT:

Airless Spray	**For dft applications between 75-125µ**	**For dft applications between 125-300µ**
Nozzle Size	: 0.33mm (13 thou)	0.38mm (15 thou)
Fan Angle	: 40°	40°
Operating Pressure	: 155kg/cm^2 (2200 psi)	155kg/cm^2 (2200 psi)

The airless spray details given above are intended as a guide only. Details such as fluid hose length and diameter, paint temperature and job shape and size all have an effect on the spray tip and operating pressure chosen. However, the operating pressure should be the lowest possible consistent with satisfactory atomisation. As conditions will vary from job to job, it is the applicators' responsibility to ensure that the equipment in use has been set up to give the best results. If in doubt Leighs Customer Service Department should be consulted. For MIO shades, use the 125-300µm recommendations.

Conventional Spray

Nozzle Size : 1.27mm (50 thou)
Atomising Pressure : 2.8kg/cm^2 (40 psi)
Fluid Pressure : 0.4kg/cm^2 (6 psi)

The details of atomising pressure, fluid pressure and nozzle size are given as a guide. It may be found that slight variations of pressure will provide optimum atomisation in some circumstances according to the set up in use. Atomising air pressure depends on the air cap in use and the fluid pressure depends on the length of line and direction of feed i.e. horizontal or vertical.
For application by conventional spray, it may be necessary to thin the paint by the addition of up to 10% Leighs Cleanser/Thinner No. 2. Where thinning has been carried out the wet film thickness must be adjusted accordingly.

Brush and Roller

The material is suitable for brush and roller application. Application of more than one coat may be necessary to give equivalent dry film thickness to a single spray applied coat.

APPLICATION CONDITIONS AND OVERCOATING:

This material should preferably be applied at temperatures in excess of 10°C. Relative humidity should not exceed 90% and in these conditions good ventilation is essential. Substrate temperature should be at least 3°C above the dew point and always above 0°C.
At application temperatures below 10°C, drying and curing times will be significantly extended, and spraying characteristics may be impaired.
Application at ambient air temperatures below 5°C is not recommended.
In order to achieve optimum water and chemical resistance, temperature needs to be maintained above 10°C during curing.
If it is desired to overcoat outside the times stated on the data sheet, please seek advice of Leighs Customer Service Department.
For full notes, see data sheet entitled 'Spreading Rates and Overcoating Times'.

ADDITIONAL NOTES:

Drying times, curing times and pot life should be considered as a guide only.
The curing reaction of epoxies commences immediately the two components are mixed, and since the reaction is dependent on temperature, the curing time and pot life will be approximately halved by a 10°C increase in temperature and doubled by a 10°C decrease in temperature.

Epoxy Coatings - Colour Stability:

Variable colour stability is a feature of epoxy materials which tend to yellow and darken with age whether used on internal or external areas. Therefore any areas touched-up and repaired with the same colour at a later date may be obvious due to this colour change.
When epoxy materials are exposed to ultra-violet light a surface chalking effect will develop. This phenomenon results in loss of gloss and a fine powder coating at the surface which may give rise to colour variation depending on the aspect of the steelwork. This effect in no way detracts from the performance of the system.

Epoxy Coatings - Tropical Use

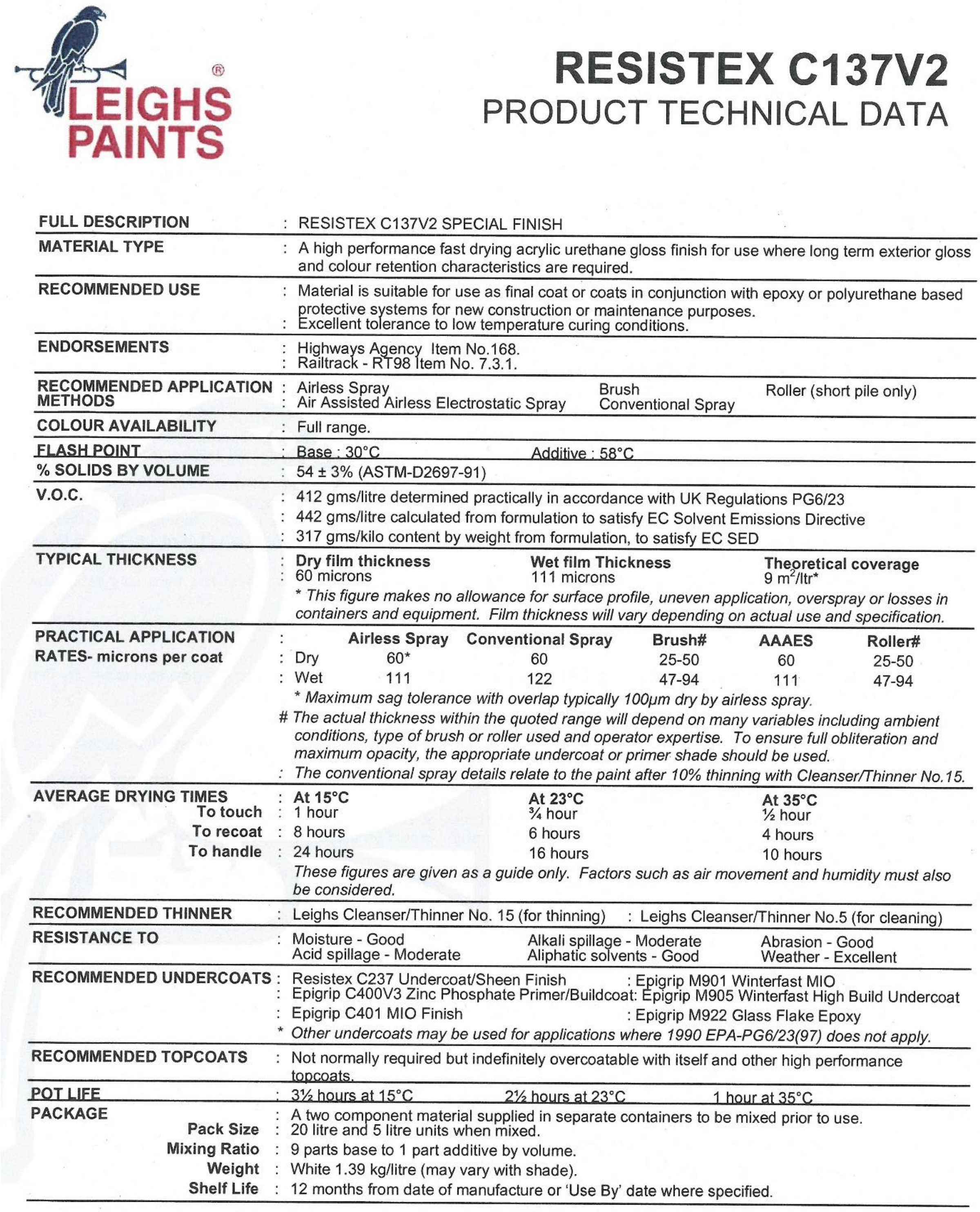
Epoxy paints at the time of mixing should not exceed a temperature of 35°C. At this temperature the pot life will be approximately halved. Use of these products outside of the pot life may result in inferior adhesion properties even if the materials appear fit for application. Thinning the mixed product will not alleviate this problem.
The maximum air and substrate temperature for application is 50°C providing conditions allow satisfactory application and film formation. If the air and substrate temperatures exceed 50°C and epoxy coatings are applied under these conditions, paint film defects such as dry spray, bubbling and pinholing etc. can occur within the coating.
Numerical values quoted for physical data may vary slightly from batch to batch.

HEALTH AND SAFETY:

Consult Product Health and Safety Data Sheet for information on safe storage, handling and application of this product.

9.5 Appendix 5: Leighs Resistex C137V2 product technical data

Leighs Resistex topcoat manufacturer datasheet.



LEIGHS® PAINTS

RESISTEX C137V2
PRODUCT TECHNICAL DATA

FULL DESCRIPTION : RESISTEX C137V2 SPECIAL FINISH

MATERIAL TYPE : A high performance fast drying acrylic urethane gloss finish for use where long term exterior gloss and colour retention characteristics are required.

RECOMMENDED USE : Material is suitable for use as final coat or coats in conjunction with epoxy or polyurethane based protective systems for new construction or maintenance purposes.
: Excellent tolerance to low temperature curing conditions.

ENDORSEMENTS : Highways Agency Item No.168.
: Railtrack - RT98 Item No. 7.3.1.

RECOMMENDED APPLICATION METHODS : Airless Spray / Brush / Roller (short pile only)
: Air Assisted Airless Electrostatic Spray / Conventional Spray

COLOUR AVAILABILITY : Full range.

FLASH POINT : Base : 30°C Additive : 58°C

% SOLIDS BY VOLUME : 54 ± 3% (ASTM-D2697-91)

V.O.C. : 412 gms/litre determined practically in accordance with UK Regulations PG6/23
: 442 gms/litre calculated from formulation to satisfy EC Solvent Emissions Directive
: 317 gms/kilo content by weight from formulation, to satisfy EC SED

TYPICAL THICKNESS

Dry film thickness	Wet film Thickness	Theoretical coverage
60 microns	111 microns	9 m^2/ltr*

** This figure makes no allowance for surface profile, uneven application, overspray or losses in containers and equipment. Film thickness will vary depending on actual use and specification.*

PRACTICAL APPLICATION RATES- microns per coat

	Airless Spray	Conventional Spray	Brush#	AAAES	Roller#
Dry	60*	60	25-50	60	25-50
Wet	111	122	47-94	111	47-94

** Maximum sag tolerance with overlap typically 100µm dry by airless spray.*

 # The actual thickness within the quoted range will depend on many variables including ambient conditions, type of brush or roller used and operator expertise. To ensure full obliteration and maximum opacity, the appropriate undercoat or primer shade should be used.

: The conventional spray details relate to the paint after 10% thinning with Cleanser/Thinner No.15.

AVERAGE DRYING TIMES

	At 15°C	At 23°C	At 35°C
To touch	1 hour	¾ hour	½ hour
To recoat	8 hours	6 hours	4 hours
To handle	24 hours	16 hours	10 hours

These figures are given as a guide only. Factors such as air movement and humidity must also be considered.

RECOMMENDED THINNER : Leighs Cleanser/Thinner No. 15 (for thinning) : Leighs Cleanser/Thinner No.5 (for cleaning)

RESISTANCE TO : Moisture - Good / Alkali spillage - Moderate / Abrasion - Good
Acid spillage - Moderate / Aliphatic solvents - Good / Weather - Excellent

RECOMMENDED UNDERCOATS : Resistex C237 Undercoat/Sheen Finish : Epigrip M901 Winterfast MIO
: Epigrip C400V3 Zinc Phosphate Primer/Buildcoat: Epigrip M905 Winterfast High Build Undercoat
: Epigrip C401 MIO Finish : Epigrip M922 Glass Flake Epoxy
** Other undercoats may be used for applications where 1990 EPA-PG6/23(97) does not apply.*

RECOMMENDED TOPCOATS : Not normally required but indefinitely overcoatable with itself and other high performance topcoats.

POT LIFE : 3½ hours at 15°C 2½ hours at 23°C 1 hour at 35°C

PACKAGE : A two component material supplied in separate containers to be mixed prior to use.
Pack Size : 20 litre and 5 litre units when mixed.
Mixing Ratio : 9 parts base to 1 part additive by volume.
Weight : White 1.39 kg/litre (may vary with shade).
Shelf Life : 12 months from date of manufacture or 'Use By' date where specified.

SURFACE PREPARATION:

Ensure surfaces to be coated are clean, dry and free from all surface contamination.

APPLICATION EQUIPMENT:

Airless Spray

Nozzle Size : 0.33mm (13 thou)
Fan Angle : 65°
Operating Pressure : 210kg/cm^2 (3000 psi)

Air Assisted Airless Electrostatic Spray

Nozzle Size : 0.33mm (13 thou)
Fan Angle : 40°
Operating Pressure : 210kg/cm^2 (3000 psi)
Air Atomisation : 2-3 Bar
Voltage : 85kv

The airless spray details given above are intended as a guide only. Details such as fluid hose length and diameter, paint temperature and job shape and size all have an effect on the spray tip and operating pressure chosen. However, the operating pressure should be the lowest possible consistent with satisfactory atomisation. As conditions will vary from job to job, it is the applicators' responsibility to ensure that the equipment in use has been set up to give the best results. If in doubt Leighs Customer Service Department should be consulted.

For C137V2 R8106 shade only, a nozzle size of 0.38-0.43 mm (15-17 thou) is recommended.

Conventional Spray

Nozzle Size : 1.27mm (50 thou)
Atomising Pressure : 3.5kg/cm^2 (50 psi)
Fluid Pressure : 0.7kg/cm^2 (10 psi)

The details of atomising pressure, fluid pressure and nozzle size are given as a guide. It may be found that slight variations of pressure will provide optimum atomisation in some circumstances according to the set up in use. Atomising air pressure depends on the air cap in use and the fluid pressure depends on the length of line and direction of feed i.e. horizontal or vertical.

For application by conventional spray thin up to 10% with Leighs Cleanser/Thinner No.15. Wet film thickness should be adjusted accordingly.

NB - Thinning will affect VOC compliance.

Brush

The material is suitable for brush application. Application of more than one coat may be necessary to give equivalent dry film thickness to a single spray applied coat.

Roller

The material is suitable for roller application using a short pile roller. Application of more than one coat may be necessary to give equivalent dry film thickness to a single spray applied coat.

APPLICATION CONDITIONS AND OVERCOATING:

This material should preferably be applied at temperatures in excess of 10°C. In conditions of high relative humidity, ie 80-85% good ventilation conditions are essential. Substrate temperature should be at least 3°C above the dew point and always above 0°C.

At application temperatures below 10°C, drying and curing times will be significantly extended, and spraying characteristics may be impaired.

Application at ambient air temperatures below 5°C is not recommended.

In order to achieve optimum water and chemical resistance, temperature needs to be maintained above 10°C during curing.

If it is desired to overcoat outside the times stated on the data sheet, please seek advice of Leighs Customer Service Department.

For full notes, see data sheet entitled 'Spreading Rates and Overcoating Times'.

ADDITIONAL NOTES:

Drying times, curing times and pot life should be considered as a guide only.

The curing reaction of the material commences immediately the two components are mixed, and since the reaction is dependent on temperature, the curing time and pot life will be approximately halved by a 10°C increase in temperature and doubled by a 10°C decrease in temperature.

Storage at high temperatures will affect build properties.

Certain shades for example, lead free yellows and reds may require additional coats to achieve full opacity.

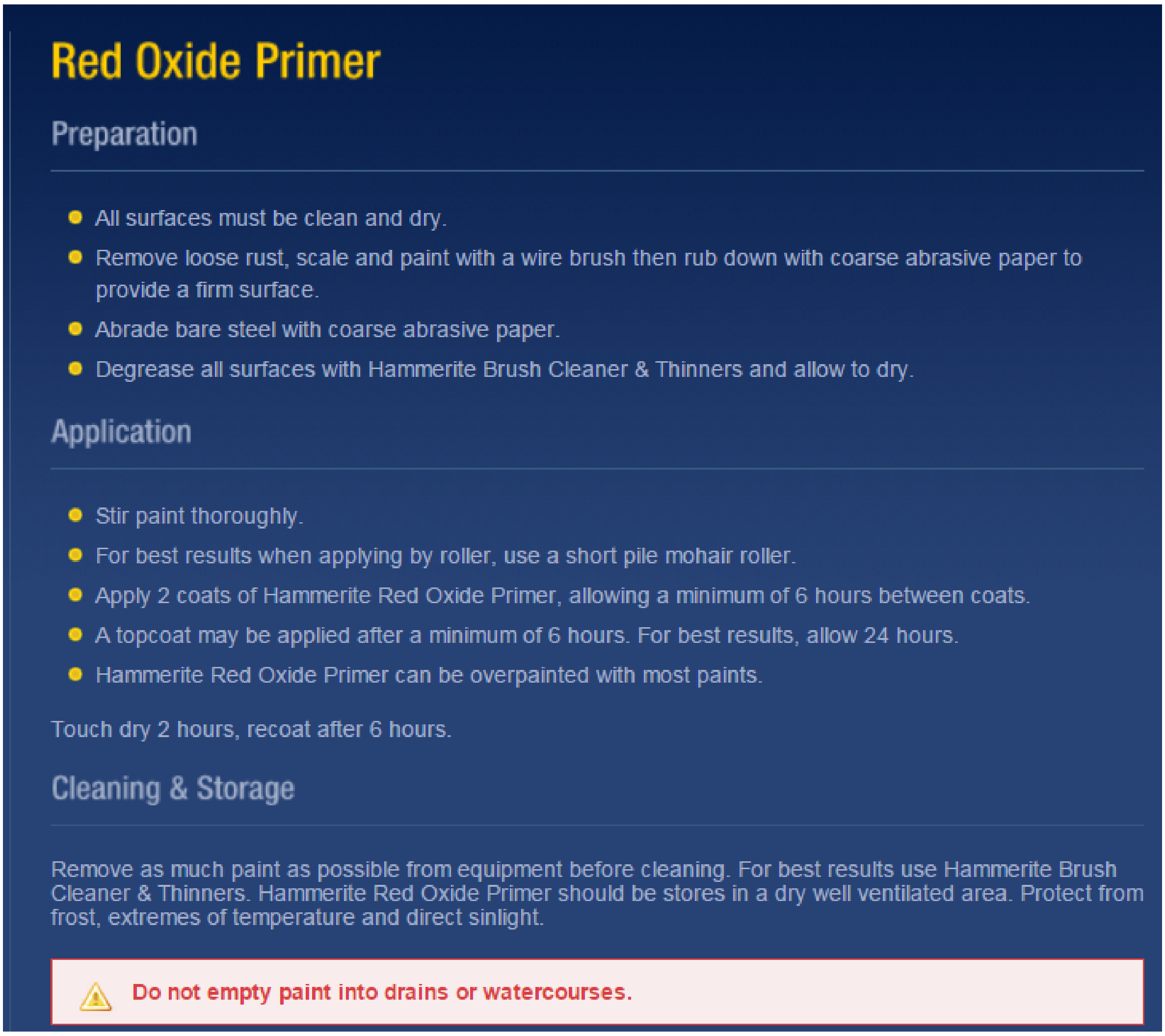
Numerical values quoted for physical data may vary slightly from batch to batch.

HEALTH AND SAFETY:

Consult Product Health and Safety Data Sheet for information on safe storage, handling and application of this product.

9.6 Appendix 6: Hammerite Red Oxide Primer datasheet

Hammerite Red Oxide Primer manufacturer datasheet.



Red Oxide Primer

Preparation

- All surfaces must be clean and dry.
- Remove loose rust, scale and paint with a wire brush then rub down with coarse abrasive paper to provide a firm surface.
- Abrade bare steel with coarse abrasive paper.
- Degrease all surfaces with Hammerite Brush Cleaner & Thinners and allow to dry.

Application

- Stir paint thoroughly.
- For best results when applying by roller, use a short pile mohair roller.
- Apply 2 coats of Hammerite Red Oxide Primer, allowing a minimum of 6 hours between coats.
- A topcoat may be applied after a minimum of 6 hours. For best results, allow 24 hours.
- Hammerite Red Oxide Primer can be overpainted with most paints.

Touch dry 2 hours, recoat after 6 hours.

Cleaning & Storage

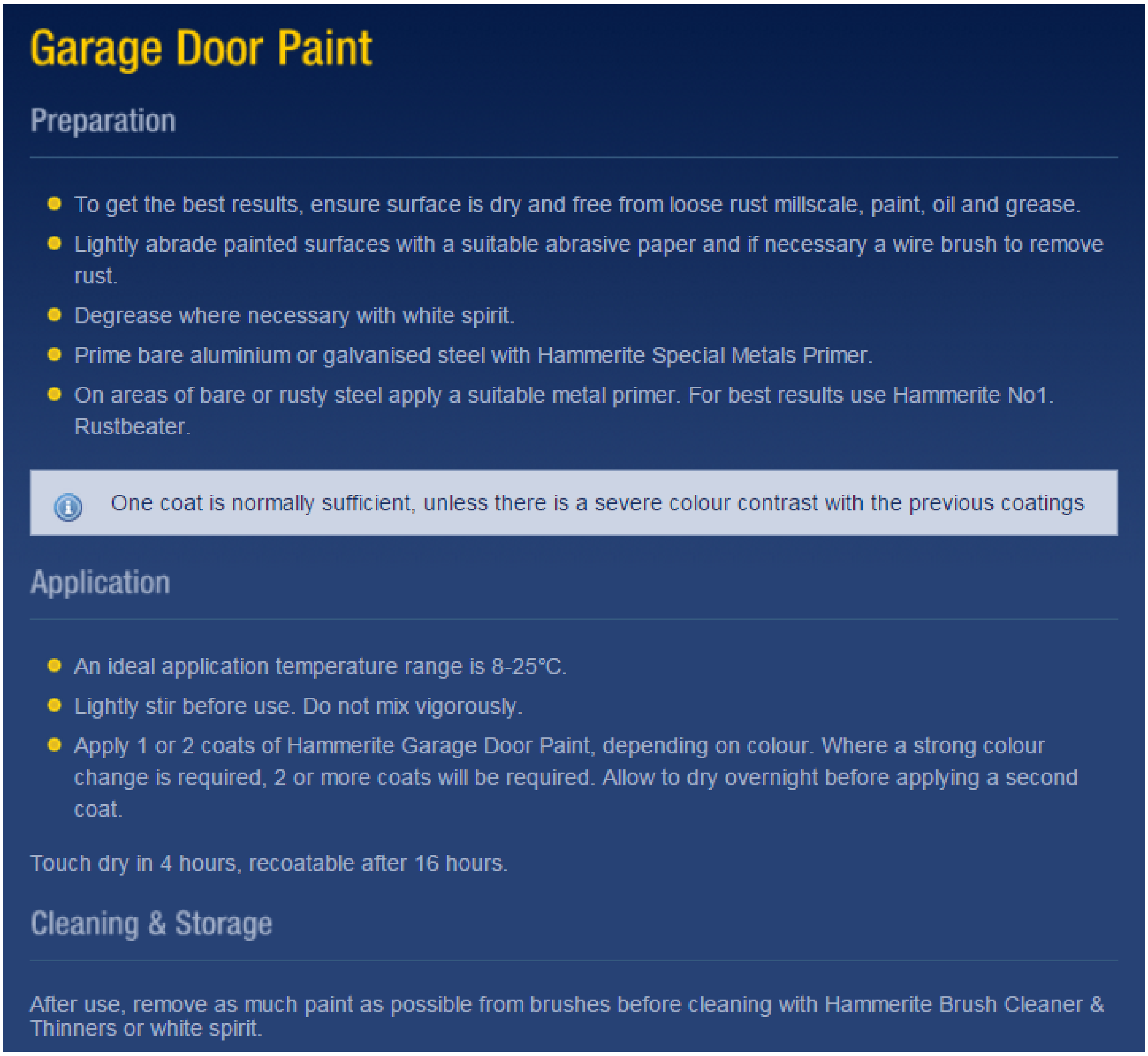
Remove as much paint as possible from equipment before cleaning. For best results use Hammerite Brush Cleaner & Thinners. Hammerite Red Oxide Primer should be stores in a dry well ventilated area. Protect from frost, extremes of temperature and direct sinlight.

⚠ Do not empty paint into drains or watercourses.

http://www.hammerite.co.uk/guide/red_oxide_primer.jsp

9.7 Appendix 7: Hammerite Garage Door datasheet

Hammerite Garage Door manufacturer datasheet.



Garage Door Paint

Preparation

- To get the best results, ensure surface is dry and free from loose rust millscale, paint, oil and grease.
- Lightly abrade painted surfaces with a suitable abrasive paper and if necessary a wire brush to remove rust.
- Degrease where necessary with white spirit.
- Prime bare aluminium or galvanised steel with Hammerite Special Metals Primer.
- On areas of bare or rusty steel apply a suitable metal primer. For best results use Hammerite No1. Rustbeater.

ⓘ One coat is normally sufficient, unless there is a severe colour contrast with the previous coatings

Application

- An ideal application temperature range is 8-25°C.
- Lightly stir before use. Do not mix vigorously.
- Apply 1 or 2 coats of Hammerite Garage Door Paint, depending on colour. Where a strong colour change is required, 2 or more coats will be required. Allow to dry overnight before applying a second coat.

Touch dry in 4 hours, recoatable after 16 hours.

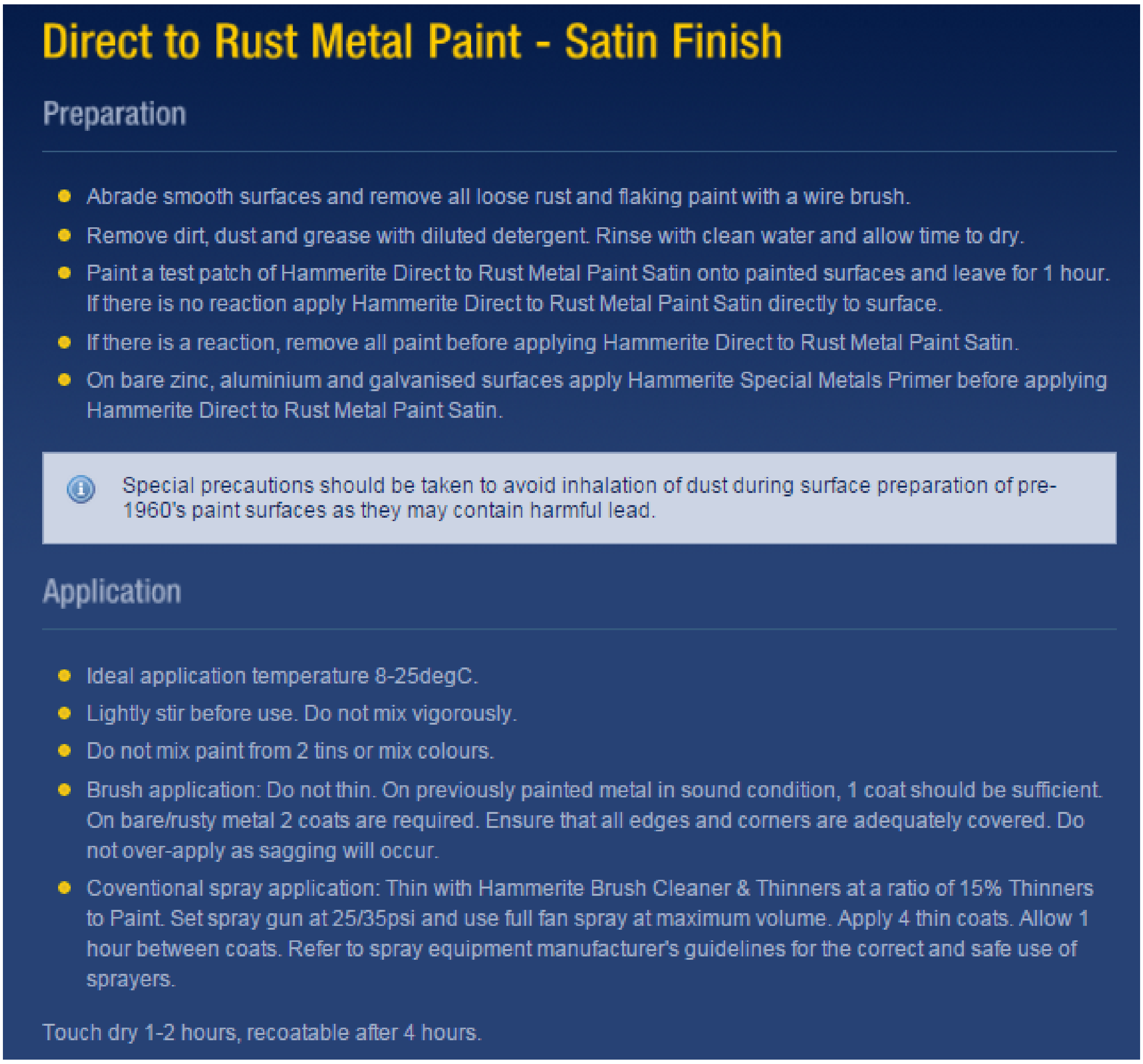
Cleaning & Storage

After use, remove as much paint as possible from brushes before cleaning with Hammerite Brush Cleaner & Thinners or white spirit.

http://www.hammerite.co.uk/guide/garage_door_paint.jsp

9.8 Appendix 8: Hammerite Direct to Rust datasheet

Hammerite Direct to Rust manufacturer datasheet.



Direct to Rust Metal Paint - Satin Finish

Preparation

- Abrade smooth surfaces and remove all loose rust and flaking paint with a wire brush.
- Remove dirt, dust and grease with diluted detergent. Rinse with clean water and allow time to dry.
- Paint a test patch of Hammerite Direct to Rust Metal Paint Satin onto painted surfaces and leave for 1 hour. If there is no reaction apply Hammerite Direct to Rust Metal Paint Satin directly to surface.
- If there is a reaction, remove all paint before applying Hammerite Direct to Rust Metal Paint Satin.
- On bare zinc, aluminium and galvanised surfaces apply Hammerite Special Metals Primer before applying Hammerite Direct to Rust Metal Paint Satin.

Special precautions should be taken to avoid inhalation of dust during surface preparation of pre-1960's paint surfaces as they may contain harmful lead.

Application

- Ideal application temperature 8-25degC.
- Lightly stir before use. Do not mix vigorously.
- Do not mix paint from 2 tins or mix colours.
- Brush application: Do not thin. On previously painted metal in sound condition, 1 coat should be sufficient. On bare/rusty metal 2 coats are required. Ensure that all edges and corners are adequately covered. Do not over-apply as sagging will occur.
- Coventional spray application: Thin with Hammerite Brush Cleaner & Thinners at a ratio of 15% Thinners to Paint. Set spray gun at 25/35psi and use full fan spray at maximum volume. Apply 4 thin coats. Allow 1 hour between coats. Refer to spray equipment manufacturer's guidelines for the correct and safe use of sprayers.

Touch dry 1-2 hours, recoatable after 4 hours.

http://www.hammerite.co.uk/guide/direct_to_rust_metal_paint_satin_finish.jsp